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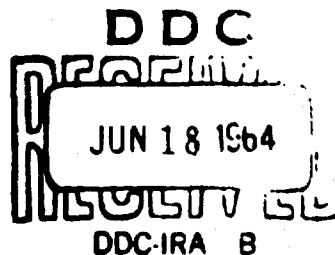
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THE AGING OF NATURAL AND SYNTHETIC
RUBBER AND RUBBER PRODUCTS

An Annotated Bibliography

Compiled by Hans Janecka

February 1964



2101 Constitution Avenue
Washington, D. C. 20418

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Division of Chemistry and Chemical Technology
National Academy of Sciences-National Research Council

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AN-253(3)

U.S. Deterioration Prevention Committee. Plastics and
Plasticizers Subcommittee.
MINUTES OF MEETING OF SUB-COMMITTEE ON PLASTICS AND PLASTICIZERS
HELD AT THE OFFICE OF NAVAL RESEARCH ON 24 OCTOBER 1946.
November 1946. 8 1.

Mr. Gerald Reinsmith submitted a list of projects sponsored by the Army Ordnance Department likely to fall within the scope of this Subcommittee. Consideration of the strippable compounds project was deferred until a Packaging Subcommittee is formed. Others submitted include investigations of (1) resistance to outdoor aging of and (2) effect of oils and fuels on molded and extruded plastics; and (3) the life of natural and synthetic rubber and rubber parts under various conditions.

It was recommended that the chairman of this Subcommittee confer with the chairman of the Electrical and Electronic Subcommittee concerning the relative authority of their respective subcommittees in the problem of organic coatings for electrical equipment.

Mr. John Steif presented a paper on the determination of the effects of fungicides on physical properties of natural and synthetic rubber when the fungicide is incorporated as a component part of the compound. Results of this investigation, still in its preliminary stages, have so far indicated (1) that natural and neoprene synthetic rubbers require no fungicide for the protection of the rubber itself, although a fungicidal treatment for GR-S may be desirable, and (2) that no fungicide tested has any pronounced deleterious effect on any of the 3 rubbers, with the exception of copper naphthenate, which has a marked effect on GR-S in retarding the rate of cure and in decreasing the strength of the vulcanized product.

Dr. J.M. Leonard presented a paper on the inherent resistance of some plasticizers to fungus attack [1,22:12,A-120]. It was suggested that similar studies of other component materials might prove valuable.

A-294

Hanson, A.C.
TROPICAL STORAGE OF RUBBER AND NEOPRENE.
U.S. Arsenal, Rock Island, Ill. Laboratory. Report 40-2983.
June 1940.

Duplicate samples of rubber (RIA 34, 54) and neoprene (RIA 157, 42N) were (1) sent to Hawaii and (2) kept at Rock Island as controls. Initial data obtained on samples from each group are given in this report. All samples passed the silver corrosion test satisfactorily. Addenda gives breaking strength and elongation results for 1, 2, and 3 yr. storage periods.

A-388(1)

U.S. Frankford Arsenal, Philadelphia, Pa. Fire Control Division.
Experimental Branch.
INVESTIGATION OF GR-S LAYTEX [SIC] AS A SUBSTITUTE FOR FXS 599
WIRE, by Rose G. Grabelsky.
Fire Control Engineering Report 1062. September 1945.

This report is the first in a series on the design and construction of an apparatus wire for use in fire control materiel. It describes the properties of a wire composed of GR-S latex primary insulation covered with a lacquered cotton braid which had been saturated with a compound containing 10% of U.S. Rubber Fungicide #3.

The weak point of this wire appears to be the ability of oil to penetrate through the lacquered braid and react with the GR-S compound. Also, prolonged immersion in water at 160 F seems to cause the coating lacquer to lose its water impermeability with resultant lowering of insulation resistance and dielectric strength. This wire will support fungus growth, indicating ineffectiveness of the fungicide used.

PDC Comment: The number of replicates employed in each test is not stated in this report. The erratic results obtained in the study of the effect of aging in water at 160 F, where the insulation resistance dropped markedly on the 6th day, returned to its original value on the 8th day, and then dropped further, suggest that the use of a greater number of specimens might give more reliable conclusions. It would also be interesting to know what the results would have been if the test had been further prolonged.

A-622(1)

Boor, Ladislav and Stanley J. Shurtleff.
SUMMARY OF SALVAGE SURVEYS AND ANALYSIS OF SERVICE PERFORMANCE OF
RAINCOATS, SYNTHETIC RESIN, SYNTHETIC RUBBER AND NATURAL RUBBER.
U.S. Quartermaster Corps. Military Planning Division. Research and
Development Branch. Coated Fabric Series. Report CF-1.
October 1947.

Analyses were made of four salvage surveys of raincoats made from fabrics coated with vinyl and polyvinyl butyral resins during 1941 - 1946. Inconclusive results led to a study of an addition 5000 coats at the Charlotte Quartermaster Depot. The second study included some natural and synthetic rubber coatings.

The inferior performance of vinyl and polyvinyl butyral coatings is confirmed. The development of stiffness is believed to be the most sensitive measure of progressive deterioration; most of the other forms of failure, such as cracking, peeling, blistering, and tearing, are associated with or follow stiffening.

Deterioration under conditions of high relative humidity has not been sufficiently emphasized or adequately evaluated. Both vinyl and polyvinyl butyral coatings support mildew growth at summer temperatures when the humidity is high, and decomposition odors at this time are noticeable. GR-S coatings show negligible or no growth under the same conditions.

Casein buttons which are often attacked by fungi should be replaced by those made of phenolic or melamine resins.

PDC Comment: Fungal damage to raincoats is discussed in previously abstracted reports from the U.S. Quartermaster Depot:

- (1) FUNGAL RESISTANCE OF COATED FABRICS. 1948. PDA 5: T 61, A-586
- (2) FUNGAL RESISTANCE TESTS. 1948. PDA 6: T 2, A-577
- (3) FUNGI ISOLATED FROM STORED RAINCOATS FROM CAMP LEE. 1948. PDA 5: T 61, A-587
- (4) A TEST TO EVALUATE DAMAGE TO COATINGS OF COATED FABRICS (RAINCOAT MATERIALS) RESULTING PRIMARILY FROM ACTIVITIES OF MICROORGANISMS. 1948. PDA 6: T 3, A-578

A-635(3)

U.S. Naval Air Material Center, Philadelphia, Pa. Aeronautical Materials Laboratory.

STABILITY OF SYNTHETIC AND AN-C-54 CEMENTS, reported by F.H. Bair. Report TED No. NAM 25335, Part III. April 1945.

A summary of the conclusions reached after making stability tests with neoprene cements, AN-C-54 types A and B cements, and a group of unclassified synthetic cements is presented.

In a container such as glass, which exerts no catalytic action on the cement, 1-day storage at 120 F is roughly equivalent to 4 - 6 days at 75 F. However, additional gelation data at 75 F are needed to establish a more precise relationship.

The stability of neoprene cements is entirely dependent upon the storage temperature. The storage life of qualified Navy Aero. Spec. C-137 Cements can be conservatively estimated to be 1 - 2, 4 - 5, and 6 - 7 mo at respective temperatures of 100 - 120 F, 75 - 90 F, and below 70 F.

Terne plate apparently affects the storage life of most neoprene cements adversely; tin plate exerts a slight effect in some cases, whereas glass is the most innocuous packaging material. The stability of AN-C-54 cements is apparently not affected by the type of container used if an accelerator accompanying the cement is packaged in a nonmetallic container.

A cement may become useless by three mechanisms, viz., by gelling due to polymerization, by drying caused by volatilization of solvents, and by loss of adhesive strength as a result of depolymerization.

The variation in stability characteristics between different lots of the same neoprene cement emphasizes the need for inspection control of cements stocked by naval supply or air stations. The inclusion of a 20-day stability test at 120 F in Navy Aero. Spec. C-137 (Cement, Synthetic, Rubber to Metal (Oil Resistant)) is advisable.

PDC Comment: It was pointed out in a previous progress report on this subject, that the AN-C-54 Type B cements are apparently the most satisfactory as far as gelling out in storage is concerned; but there is evidence that this type tends to thin out on aging and lose adhesive properties.

The limited stability of neoprene cements seems to preclude their use in life raft repair kits and/or other applications requiring a high degree of stability under adverse conditions. [STABILITY OF SYNTHETIC CEMENTS. December 1944. AN-635(2)]

A-698

U.S. Naval Shipyard, Mare Island, Calif. Rubber Laboratory.
EVALUATION OF ACCELERATED LIGHT AGING PROCEDURES WITH CARBON
ARC PARTLY ENCLOSED BY WATER-COOLED PANELS, PROGRESS REPORT
NO. 2, by A.E. Barrett.
Report 4-32. April 1948.

Specimens of soft gasket stocks of natural and synthetic rubber vulcanizates, under elongation of 0, 10, and 25%, were exposed (1) to carbon-arc radiation under conditions designed to simulate average weather conditions and (2) to natural weathering at four different locations. Tensile and appearance data were compared for natural rubber, GR-S, Perbunan 26, Hycar OR-15, Neoprene FR, Thiokol FA, GR-I, and GR-M.

The accelerated light aging procedure correlated well with weather aging for all the stocks exposed except GR-I and Thiokol FA. Further attempts to develop an accelerated light aging procedure which would incorporate all deteriorating factors in the same relative intensity as they occur in weather should be abandoned as a practical impossibility. Instead, two separate tests, an accelerated ozone aging test and an accelerated crazing test, should be designed.

The deterioration of weather-aged specimens varied considerably among exposure stations, but the relative weather resistance of the different stocks was about the same at all locations. Data on tensile strength retention showed that GR-M, Thiokol FA, and GR-I withstand natural weathering best, followed by Neoprene FR, Perbunan 26 and Hycar OR-15, GR-S, and natural rubber. For the particular exposure dates the severest conditions existed at Mare Island, followed by those at New York and Portsmouth; the deterioration of specimens exposed at Panama was particularly small, indicating a comparatively low ozone concentration, which is considered the main differentiating factor.

The weatherometer used in these investigations was a modified National Eveready Unit in which the arc was surrounded with sixteen water-cooled panels equally spaced so that about 50% of the direct radiation was blocked off of each. The standard turntable was altered so that one row of specimens could be hung vertically, centered in the horizontal plane bisecting the arc at a mean distance of 16 in. The turntable speed was changed to 11 min per revolution, and samples were water sprayed once per revolution. Of the various arcs tried, the 'C' carbon arc was best because it gave good correlation with weather aging and produced measurable changes in tensile strength in a reasonable time.

- A-836 Patton, S.U.
REPORT OF AN INVESTIGATION OF SIMULATED SERVICE LIFE CHARACTER-
ISTICS AND PERFORMANCE OF RUBBER AND SYNTHETIC RUBBER STAVE
BEARINGS FOR STERN TUBE AND STRUT SERVICE.
U.S. Naval Engineering Experiment Station, Annapolis, Md.
Report C-3330-C. October 1949.
- A-841 Fenster, Henry.
ARMY-NAVY AERONAUTICAL SPECIFICATION AN-C-54a, NATURAL RUBBER
CEMENT, QUALIFICATION TESTS UNDER.
U.S. Naval Air Material Center, Philadelphia, Pa. Aeronautical
Materials Laboratory. Report No. AML NAM AE 424707, Part II.
September 1949.
- A-849 U.S. Naval Shipyard, Mare Island, Calif. Rubber Laboratory.
PROGRESS REPORT #8 ON THE DEVELOPMENT OF PRESERVATIVES FOR
NATURAL AND SYNTHETIC RUBBER VULCANIZATES. EVALUATION OF
WILLARD PRESERVATIVES, by A.E. Barrett.
Report 64-21. October 1949.
- A-869 U.S. Naval Shipyard, Mare Island, Calif. Rubber Laboratory.
REPORT NO. 2 ON SHELF AGING, OXYGEN BOMB AGING, AND AIR OVEN
AGING OF VARIOUS ELASTOMER VULCANIZATES, by R.D. Ford.
Report 5-7. December 1949.
- A-876 U.S. Naval Shipyard, Mare Island, Calif. Rubber Laboratory.
LOW TEMPERATURE PERFORMANCE TESTS ON GASKETS IN WATERTIGHT
CLOSURES, by J.W. Hollister.
Report 107-22. December 1949.
- A-920 U.S. Naval Shipyard, Portsmouth, N.H. Materials Testing Laboratory.
FINAL REPORT ON COMPARATIVE AGING TESTS OF RUBBER AND SYNTHETIC
RUBBER GASKET STOCKS AT 194° F AND 212° F, by Frederick L. Downs.
Report RD-50AD. March 1950.
- A-921 U.S. Arsenal, Rock Island, Ill. Laboratory.
OZONE AGING OF POLYMERS, by Z.T. Ossefort.
Report 49-1236. October 1949.

The ozone resistance of various rubbers can be determined by a 6-hr test in an apparatus consisting of an ozone generator, a testing chamber, and a device for measuring ozone concentration. The reduction of stretch of the specimens, caused by ozone cracking, is a measure of the degree of ozonation, and can be used to ascertain the ozone resistance afforded by various protective coatings.

Natural rubber, GR-S, and Buna N were especially susceptible to ozone cracking and therefore could be improved by an ozone-

resistant protective coating. Of various rubber coatings tested, neoprene, polyisobutylene, Pliolite S4, and Vanderbilt Blackout Black were the most resistant to ozone attack.

For long-term storage, rubber components should be kept in an unstressed condition where possible.

A test temperature of 100 F is recommended in order to avoid refrigeration of the sample during the summer months to obtain the 70 F temperature currently specified in the ASTM D470-48T test procedure.

A-924

U.S. Naval Shipyard, Mare Island, Calif. Rubber Laboratory.
DEVELOPMENT OF AN OIL-RESISTANT GASKET STOCK WITH IMPROVED COLD
RESISTANCE TO MEET SPECIFICATION 33G5, by J.W. Hollister.
Report No. 7-14. May 1950.

A-968

U.S. Naval Shipyard, Brooklyn, N.Y. Material Laboratory.
REPORT OF INVESTIGATION OF THE APPLICABILITY OF THE GURLEY
STIFFNESS TESTER IN THE LOW TEMPERATURE EVALUATION OF NATURAL
AND SYNTHETIC ELASTOMERS.
Report 4855-10 (Final). October 1950.

The Gurley stiffness tester, although relatively simple in design and easy to operate, is not entirely suitable for evaluating low-temperature stiffness properties of natural and synthetic elastomers. The design features of the instrument do not permit measurement of angular deflection of the specimen.

Stiffness tests were conducted on neoprene, Buna S, Perbunan 26, Hevea, butyl rubber, and Thiokol FA. Samples were tested 1 hr at temperatures ranging from 75 to -40 F, and 1-94 hr at -20 F. With most samples, there was marked similarity between the shape of the curves of the modulus proportionality factors (MPF) as determined with the Gurley tester and those obtained with the Gehman stiffness tester. With Hevea stocks, however, the Gehman tester indicated a greater and earlier increase in stiffness than did the Gurley instrument. On the basis of MPF ratios, the data showed excessive deviation from the theoretical linear relationship. The MPF ratio is defined as the ratio of an MPF value determined under any condition of time and temperature to that determined under arbitrary standard conditions. It is believed that such factors as high friction between the specimen and pendulum of the Gurley device, and differences in strain time contribute appreciably to the deviations. The exact causes, however, could not be readily assigned.

MPF ratios are considered more suitable than T-values for evaluating stiffness properties of elastomers that must conform to low-temperature specifications. T-values can be derived only after making tests over a range of low temperatures, followed by graphical determination of the desired values, which most often would be below the contemplated service temperatures.

A-969

U.S. Naval Shipyard, Brooklyn, N.Y. Material Laboratory.
REPORT OF INVESTIGATION ON THE APPLICABILITY OF THE TINIUS OLSEN
STIFFNESS TESTER 6 INCH-POUND CAPACITY IN THE LOW TEMPERATURE
EVALUATION OF NATURAL AND SYNTHETIC ELASTOMERS.
Report 4855-7 (Final). October 1950.

The applicability of the Tinius Olsen stiffness tester of 6 in.-lb capacity for determining the low-temperature flexural properties of typical natural and synthetic elastomers was investigated. The elastomers tested were neoprene, Buna S, Perbunan 26, Hevea, butyl rubber, Thiokol FA, and Silastic SR-167. Short-time (1 hr) exposure tests were conducted at temperatures ranging from 75 to -40 F; long-time (22-96 hr) exposure tests were made at -20 F.

In the short-exposure tests, all the elastomers except the Hevea compounds increased substantially in modulus of elasticity as exposure temperature decreased; Perbunan 26 increased the most. Although the Hevea compounds did not change appreciably in modulus at temperatures from 75 to -35 F, they did increase in modulus at temperatures below -35 F. On long-time exposure Hevea and Thiokol FA stiffened considerably at -20 F, apparently because of polymer crystallization. After 46-hr exposure, neoprene, Hevea, butyl rubber, and particularly Perbunan 26 became leathery and decreased markedly in retained stress during a 30-sec loading period.

The Tinius Olsen stiffness tester is satisfactory for evaluating elastomeric materials with regard to relative changes in modulus resulting from aging or low temperatures, but cannot be used to determine absolute values of flex modulus, since Hooke's Law does not apply. Specimens used in the Tinius Olsen tester are of such size and shape that they are readily adapted to solvent immersion tests.

Although no general correlation between the Tinius Olsen and the Gehman stiffness tests can be established, the same general trends in low-temperature angular set were noted. The conditioning temperatures used in the Tinius Olsen tests were not sufficiently low to determine the temperature of maximum set of the elastomers. The MPF ratios calculated from short-time exposure data obtained with the Tinius Olsen, the Gehman, and the Gurley testers rate the elastomers in about the same order of merit. Tinius Olsen test data correlated better with Gurley test data than with Gehman test data. The MPF ratios based on 0-sec readings for the Tinius Olsen tester showed better correlation with data from the other testers than similar ratios based on 30-sec readings.

A low-temperature flex test using the Tinius Olsen tester is not comparable with a compression-set test. The compression test subjects specimens to strain during the entire conditioning period and is thus more representative of service conditions. A flex test, however, is suitable for materials such as hose and coated fabrics.

A-974

U.S. Arsenal, Rock Island, Ill. Laboratory.
STIFFNESS AND BRITTLINESS CHARACTERISTICS OF ELASTOMERS AT
EXTREME LOW TEMPERATURES, by R.F. Shaw.
Report No. 49-1655. December 1949.

Stiffness and brittleness tests of elastomers at low temperatures are representative of arctic service exposure conditions. Low-temperature stiffness and brittleness characteristics of sixty-three elastomer formulations were determined, using a modified Clash and Berg torsional stiffness apparatus, the standard ASTM D736 bent-loop brittleness apparatus, and a modified ASTM D746 impact brittleness apparatus. Inner-tube samples were tested at six laboratories with good correlation of results between laboratories for equal exposure periods. Best correlation was obtained with the Clash and Berg test.

For determining low-temperature flexibility, the Clash and Berg torsional stiffness method is recommended; for low-temperature brittleness, the impact brittleness test is most suitable. Both methods should be adopted in all Army specifications for determining low-temperature brittleness of rubber articles. A minimum of 24-hr exposure in air at the test temperature of -65 to -70 F is needed before testing.

Of the three tests, the Clash and Berg test was the most severe, the bent-loop test, the least. With one exception, the T200° torsion values were obtained at temperatures approximately 5 degrees higher in the Clash and Berg test than in the D746 brittleness test.

The modified Clash and Berg apparatus utilizes a sample holder that does not require holes in the sample for gripping, and a liquid cooling medium that can be maintained at a definite temperature (± 1 F) for extended periods of time. The ASTM D746 impact brittleness apparatus was modified to allow mounting of the apparatus in a cold box cooled by dry ice instead of the conventional liquid bath, thus permitting a longer pretest conditioning period. The specimen holder was changed to allow consecutive testing of five specimens.

A-977

U.S. Quartermaster Depot, Philadelphia, Pa. Chemicals and
Plastics Laboratories.
DEVELOPMENTS IN COATED FABRICS AND FILMS BY THE QUARTERMASTER CORPS,
by Ladislav Boor.
Research Service Test Report C&P-150-F&CF. August 1950.

A-1009

U.S. Naval Shipyard, Brooklyn, N.Y. Material Laboratory.
REPORT OF EVALUATION OF BUNA-N SYNTHETIC RUBBER DRUM GASKETS
SUBMITTED BY B.F. GOODRICH CO.
Lab. Project 5094-12, Final Report. January 1951.

- A-1012 U.S. Naval Shipyard, Brooklyn, N.Y. Material Laboratory.
REPORT OF INVESTIGATION OF THE APPLICABILITY OF THE MATERIAL
LABORATORY-ADMIRALTY INDENTOMETER IN THE LOW TEMPERATURE
EVALUATION OF NATURAL AND SYNTHETIC ELASTOMERS.
Lab. Project 4855-2A (Final Report). December 1950.
- The Material Laboratory Admiralty indentometer possesses good constructional features and can be used to advantage in measuring low-temperature indentation of elastomers. The indentation data correlate well with data obtained in comparable tests on the same elastomers using the Pusey and Jones plastometer, the ASTM hardness tester, and the Admiralty rubber meter. The data also correlate well with those obtained in stiffness tests using the Gehman and the U.S. Rubber Co. torsional devices.
- The Material Laboratory indentometer is a modification of the British Admiralty rubber meter. The revised instrument, which conforms to various Federal, Bureau of Ships, and Navy specifications for rubber goods, has the following changes: (1) minor load is changed to 90 g by adjustment of the dial indicator spring, (2) major load is increased to 1000 g, and (3) diameter of hemispherical indenter foot is increased to 0.125 in. As shown by comparing the rate of change of MPF values, these modifications do not affect the desirable operating characteristics of the British instrument.
- A-1022 U.S. Naval Shipyard, Brooklyn, N.Y. Material Laboratory.
REPORT OF EVALUATION OF FUEL AND LUBRICANT CONTAINER SYNTHETIC
RUBBER GASKETS SUBMITTED BY FIRESTONE INDUSTRIAL PRODUCTS CO.
Lab. Project 5094-9 (Final Report). December 1950.
- A-1025 U.S. Puget Sound Naval Shipyard, Bremerton, Wash. Production Dept.
Laboratory Branch.
EXAMINATION OF NATURAL AND SYNTHETIC RUBBER PRODUCTS, USS
SUSSEX (AK 213) (NS 033-082).
Technical Report No. 229/R-225-50. August 1950.
- A-1035 U.S. Puget Sound Naval Shipyard, Bremerton, Wash. Material Laboratory.
EXAMINATION OF NATURAL AND SYNTHETIC RUBBER PRODUCTS, USS
QUINCY (CA 71) (NS 033-082), signed by W.B. Lew and J.F. Mills.
Report 229/R-188-49. December 1949.
- A-1043 U.S. Naval Shipyard, Brooklyn, N.Y. Material Laboratory.
REPORT OF EVALUATION OF BUNA-N SYNTHETIC RUBBER DRUM GASKETS
SUBMITTED BY HERESITE AND CHEMICAL COMPANY.
Lab. Project 5094-11 (Final Report). February 1951.
- A-1049 U.S. Naval Shipyard, Brooklyn, N.Y. Material Laboratory.
REPORT OF EVALUATION OF BUNA-N SYNTHETIC RUBBER DRUM GASKETS
SUBMITTED BY UNITED STATES RUBBER CO.
Lab. Project 5094-13 (Final Report). March 1951.

A-1056

U.S. Arsenal, Rock Island, Ill. Laboratory.
EVALUATION OF SERVICE TESTED, AGED ORDNANCE TRUCK TIRES,
by S.R. Adams.
Report No. 50-3354. December 1950.

Service-tested, aged ordnance tires were evaluated for the purpose of determining the life expectancy of aged, unused tires. Test results showed that the deterioration of physical properties such as tensile strength, elongation, and hardness is not an adequate criterion for determining life expectancy. A few deep ozone cracks in tires are more likely to cause failure than many small checks. Early blowout failures in service are common among tires that display severe ozone cracking. The growth of ozone cracks depends on stresses such as static pressure or dynamic flexing to which tires are subjected.

Rubber tires aged 5-8 yr in open storage decreased 15-30% in tensile strength and 40-60% in elongation and increased 6-10 points in Durometer A hardness. The decrease in tensile strength was about 9% greater for non-failure tires than for failure tires. Some aged tires increased in tensile strength indicating that the common practice of using tensile decrease as a measure of deterioration is not justified.

The tensile strength of rubber tires heat aged at 158 F for 7 days most nearly duplicated the tensile strength of tires aged in the open for 5 yr. The decrease in elongation of tires aged naturally for 5-8 yr was approximately duplicated by the decrease in elongation caused by heat aging at 212 F for 70 hr. With the exception of a thin surface layer, rubber in an aged tire appeared to be deteriorated evenly throughout its cross section. Since neither heat aging test duplicated all of the physical properties occurring in natural aging, the two aging mechanisms must be different.

Wax incorporated in a rubber gives considerable static protection against ozone cracking. Protective coatings containing Vanderbilt's Black Out Black, Thiokol, or neoprene were also satisfactory. A butyl sheath held by aluminum rings to the rim of the wheel of the stored tire extends service life. Waterproof paper wrapped around tires also affords protection which is attributed to the partial exclusion of ozone and to the deactivating effect of the cellulose in the vicinity of rubber.

PDC Comment: Another article on the subject has been abstracted at the Center. [A. Nelson et al, THE EFFECT OF ATMOSPHERIC OZONE ON TIRES DURING STORAGE, Rubber Age (N.Y.) 66:659-662 (March 1950); PDA 8:Plas 182, G-6032]

A-1061

U.S. Naval Shipyard, Brooklyn, N.Y. Material Laboratory.
REPORT OF EVALUATION OF BUNA N SYNTHETIC RUBBER DRUM GASKETS
SUBMITTED BY STALWART RUBBER COMPANY.
Lab. Project 5094-15 (Final Report). April 1951.

A-1064

U.S. Naval Shipyard, Mare Island, Calif. Rubber Laboratory.
DEVELOPMENT OF GR-S SOFT GASKET STOCKS COMPLYING WITH
SPECIFICATION MIL-R-900A, by J.W. Hollister.
Report No. 45-21. December 1950.

Of six GR-S soft gasket stocks tested, two based on GR-S grade X-419 (E-162-1100 and E-162-1472) and two based on standard grade GR-S met the requirements of Mil. Spec. MIL-R-900A given below.

The first three stocks contained 40 parts Philblack A and 1 part Heliozone per 100 parts GR-S; the fourth stock contained 30 parts Philblack A, 15 parts Statex B (fine furnace black), and 1 part nickel dibutyldithiocarbamate per 100 parts GR-S. Two stocks, one based on standard and one on X-419 grade GR-S, did not meet the requirements for retention of tensile strength after accelerated light aging. All six stocks contained 20 parts Adipol 2EH or Flexol TOF as plasticizer.

Specimens for hot compression set tests were cured 10, 20, 30, and 40 min at 310 F. The optimum cure was selected as the point where the hot compression set was 30%.

All tests were conducted according to the specification except that the dial micrometer used was modified to exert a downward force of 0.5 instead of 3 oz, and the cold compression set tests were conducted in methanol rather than in air or carbon dioxide.

MIL-R-900A stipulates the following minimum values: 100 psi tensile strength, 300% ultimate elongation, 1.4 mm Pusey-Jones indentation for 0.5-in. thick samples; retention of 75% initial tensile strength and 70% ultimate elongations and 1.15-mm indentation after 46 hr oven-aging at 194 F; 1-mm indentation after 94 hr at -35 F; retentions of 75% tensile and 65% elongation after 100 hr semi-filtered light exposure; no delamination after 24 hr in benzene at 82 F; 95 psi initial sealing pressure, and 70 psi after 48 hr aging at 158 F. The following maximum limits are specified: 1.4 sp gr, 40% compression set after 46 hr at 194 F, 75% set after 94 hr at -35 F ten sec after release and 45% set 30 min after release; 25 g load to deflect 1 in. and 35 g to deflect 2 in. after 3 hr at -20 F; 5% swelling after 24 hr in 82 F water, and 0.5% swelling after 1 hr in boiling water.

A-1072

U.S. Naval Shipyard, Mare Island, Calif. Rubber Laboratory.
DEVELOPMENT OF NEOPRENE AND HEVEA-RUBBER CAISSON GASKETS COMPLYING
WITH SPECIFICATION 3309, by A.E. Barrett.
Report No. 20-4. March 1951.

A-1073

U.S. Naval Shipyard, Mare Island, Calif. Rubber Laboratory.
EVALUATION OF EXPERIMENTAL BUTADIENE/STYRENE COPOLYMERS FOR GASKET
SERVICE AT -35°F, by J.W. Hollister.
Report No. 49-43. February 1951.

A-1074

U.S. Naval Shipyard, Mare Island, Calif. Rubber Laboratory.
AN INVESTIGATION OF THE REPRODUCIBILITY OF THE ACCELERATED LIGHT
AGING TEST, by J.W. Hollister.
Report No. 4-43. March 1951.

- A-1086 U.S. Puget Sound Naval Shipyard, Bremerton, Wash. Production Dept. Laboratory Branch.
EXAMINATION OF NATURAL AND SYNTHETIC RUBBER PRODUCTS; USS
NAMAKAGON (AOG 53) (NS 033-082), signed: W.B. Lew, J.F. Mills,
and C.L. Fears.
Technical Report No. 229/R-244-51. April 1951.
- A-1092 U.S. Naval Shipyard, Brooklyn, N.Y. Material Laboratory.
REPORT OF EVALUATION OF GR-S SYNTHETIC RUBBER GASKET MATERIAL
SUBMITTED BY MARE ISLAND NAVAL SHIPYARD.
Lab. Project 4598-207 (Final Report). June 1951.
- A-1094 U.S. Naval Shipyard, Mare Island, Calif. Rubber Laboratory.
COMPARISON OF VARIOUS NITRILE RUBBERS IN A SOFT GASKET FORMULATION,
by J.W. Hollister.
Report No. 7-15. December 1950.
- A-1110 U.S. Arsenal, Rock Island, Ill. Laboratory.
PNEUMATIC EQUILIBRATOR PACKINGS FOR OPERATION AT SUB-ZERO AND
NORMAL TEMPERATURES, by W.E. Peterson.
Report No. 51-981. May 1951.
- A-1114 U.S. Naval Shipyard, Mare Island, Calif. Rubber Laboratory.
EVALUATION OF SOFT GASKET STOCK NO: 4247 SUBMITTED BY THE
RUBBERCRAFT CORPORATION OF CALIFORNIA, by J.W. Hollister.
Report No. 35-2. May 1951.
- A-1125 U.S. Naval Shipyard, Mare Island, Calif. Rubber Laboratory.
LOW TEMPERATURE PROPERTIES OF BLENDS OF NEOPRENE RT WITH OTHER
ELASTOMERS, by R.R. James.
Report No. 46-21. June 1951.
- A-1164 U.S. Naval Shipyard, Mare Island, Calif. Rubber Laboratory.
EVALUATION OF EXPERIMENTAL BUTADIENE/ACRYLATE, BUTADIENE, AND
BUTADIENE/STYRENE RUBBERS FOR GASKET SERVICE AT -35°F,
by J.W. Hollister and R.E. Morris.
Report No. 69-44. December 1951.

The low-temperature behavior of thirteen experimental rubbers was compared with GR-S 10 using a soft gasket recipe. Nine of the experimental rubbers were made with butadiene and various acrylates and polymerized at 14, 41, or 122 F. Of the remaining four rubbers, one was butadiene and three were butadiene-styrene, all sodium-catalyzed at 168 F.

Compared with GR-S 10, the butadiene-acrylate rubbers were generally more cold resistant from the standpoint of cold compression set and change in hardness when cooled to -35 F. In most instances

they had somewhat poorer tensile properties. The 70/30 butadiene-butyl acrylate copolymer at 41 F was the best compromise between tensile properties and cold resistance.

The sodium-catalyzed butadiene rubber had slightly better cold resistance but much poorer tensile properties than GR-S 10. The sodium-catalyzed butadiene-styrene rubbers had poorer tensile properties and poorer cold resistance than GR-S 10.

Test stock comprised 100 parts polymer, 5 zinc oxide, 30 Philblack A, 15 Statex B, 1 Heliozone, 20 Flexol TOF, 1 methyl Tuads, and 1 sulfur.

PDC Comment: Another report on the subject from the same source has been abstracted at the Center. [THE COLD RESISTANCE OF VULCANIZATES PREPARED FROM VARIOUS BUTADIENE AND BUTADIENE-STYRENE ELASTOMERS, Report 69-34, October 1949, PDA 8:Plas 132, A-845.]

A-1180

U.S. Naval Engineering Experiment Station, Annapolis, Md.
LOW TEMPERATURE CHARACTERISTICS OF SYNTHETIC RUBBER GASKET MATERIAL,
by John S. Post.
Report C-3392. March 1952.

The characteristics of synthetic rubber gasket material were investigated at 20 F intervals from 60 F to -60 F. Basic rubbers tested were polychloroprene, butadiene-styrene and butadiene-acrylonitrile. The effect of temperature on compression set, flexibility, brittleness, seal aging, and hardness was determined on samples received from five manufacturers.

With decreasing temperature, all of the materials depreciated in one or more physical properties. No one manufacturer's material was superior in all tests. A butadiene-acrylonitrile showed the best low-temperature resistance of the compounds which complied with specifications. The butyl-base material was the best of those which did not comply. Wire-inserted or cloth-inserted samples depreciated more than plain rubber samples.

The hardest materials showed the least change. The polychloroprene-base, the butadiene-acrylonitrile base, and some of the butadiene-styrene base materials showed evidence of crystallization or second-order transition at approximately -40 F. The softer butadiene-styrene and the butyl-base materials did not exhibit second-order transition even at -60 F, indicating that the hardness properties of the butyl-base materials appear best for low-temperature service.

A-1185

U.S. Naval Shipyard, Mare Island, Calif. Rubber Laboratory.
DEVELOPMENT OF AN OIL-RESISTANT GASKET STOCK FOR LOW-TEMPERATURE APPLICATIONS, by J. Oser and J.W. Hollister.
Report No. 7-19. May 1952.

A storage-stable, oil-resistant gasket stock was developed that complies with the low-temperature compression set and hardness requirements of Spec. MIL-R-900A and with modified requirements of Spec. MIL-G-2765 (tensile strength 1000 psi minimum, ultimate

elongation 300% minimum). This gasket stock, E-9-480, comprises 90 parts Paracril 18-80, 10 Neoprene FR, 5 zinc oxide, 35 Pelletex, 40 P-33, 15 TP-90B, 15 KP-140, 1 stearic acid, 1.4 Methyl Tuads, and 0.8 sulfur. It has a tensile strength of 1350 psi, 440% elongation, 890 psi modulus at 300% elongation, 1.51 mm P & J 1/2-in. indentation, 13% compression set after 46 hr at 194 F, 71% set after 94 hr at -35 F within 10 sec and 33% within 30 min, and a Mooney scorch value of 55 min at 212 F, using a small rotor. It is not known whether this formulation will perform as well when mixed on industrial equipment as when mixed in the laboratory.

In this study 10% plasticizers were evaluated for their effects on the compression set of one basic Paracril 18-80 stock. Eight plasticizers yielding compression sets in the range 59-69% were further studied on oil-resistant Paracril 18-80 and its blends with Neoprene FR.

Paracril 18-80 stocks containing soluble or insoluble sulfur in excess of 0.8 part sulfur per 100 parts rubber cannot be relied upon to be storage stable. Stocks with 0.8 parts sulfur or less did not develop granulation and did not deteriorate in tensile properties after 7 wk at 80 F.

A-1219

U.S. Naval Shipyard, Mare Island, Calif. Rubber Laboratory.
EVALUATION OF HYCAR 1014 FOR COMPOUNDING OIL-RESISTANT COLD-
RESISTANT GASKETS, by Jacob Oser.
Report No. 7-22. August 1952.

Hycar 1014, a nitrile rubber recently made commercially available, was tested for its suitability in oil-resistant gaskets that meet the low-temperature requirements of specification MIL-R-900A and the requirements of specification MIL-G-2765, including the modified limits of 1000 psi minimum tensile strength and of 300% minimum ultimate elongation. Two Hycar 1014 stocks complied with these requirements but were marginal in retention of tensile strength after immersion in SR-6 aromatic fluid. The properties of these stocks were substantially the same as those of similarly compounded Paracril 18-80 stocks. In contrast to Paracril 18-80, however, it is not necessary to compound Hycar 1014 with Neoprene FR in order to obtain adequate cold resistance.

A-1244

U.S. Arsenal, Rock Island, Ill. Laboratory.
FIVE YEAR SUMMARY OF THE FIRESTONE-CASE AGING CONTRACT, by
John E. Maurer.
Report No. 53-2371. June 1953.

A-1245

U.S. Arsenal, Rock Island, Ill. Laboratory.
ORDNANCE CORPS PROGRAM TO PREVENT THE DETERIORATION OF ELASTOMERS,
by R.F. Shaw.
Report No. 53-3307. August 1953.

The most severe deterioration agents of elastomers are ozone, heat, and oxygen in that order.

Neoprene, Butyl, Thiokol, silicone, Hypalon, and polyacrylate rubbers, and vinyl, polyethylene, and Teflon plastics are the most resistant to ozone. Polymers based on butadiene or isoprene, such as GR-S and nitrile rubbers, as well as natural rubber are the most susceptible to ozone cracking. The time to first crack decreases as the rubber is stressed from 5 to 100%. Unstressed rubber is not subject to ozone cracking at room temperatures. The ozone cracking of tires is less severe under dynamic conditions than during static storage, and it is independent of the rate of dynamic flexing from 50 to 180 cpm. The most severe ozone cracking occurs at 100 F, decreasing above and below this temperature. The optimum concentration of ozone for accelerated tests is 0.25-0.60 ppm, but the results show no correlation with outdoor tests in which atmospheric ozone concentrations vary from 0.0 to 0.5 ppm.

Stressed rubber does not crack in atmospheres containing nitrous oxide or nitrogen dioxide, but stressed rubber exposed to oxygen for 12 wk at 158 F develops typical ozone cracks.

Exposure of rubber to light prior to ozone exposure produces a surface film which increases the resistance to ozone. Protective coatings of 4-8 mil neoprene or 15-20 mil vinyl polymer prevent ozone cracking as long as they are not ruptured, but they are costly. Wrappers based on polymer films or rubber-impregnated paper envelopes prevent cracking by exclusion of air. Veneers made from ozone-resistant polymers are satisfactory on large-size truck tires. Rubber compositions are also protected from ozone by incorporating 3-15 parts of certain waxes or, preferably, chemical inhibitors. Effective antioxidants for GR-S polymers are 3-5 parts of certain amines such as N,N'-di-sec-butylbenzidine or p-phenylenediamine and 4,4'-diaminodiphenylmethane. Thus, 90/10 GR-S specimens containing 2 parts of N,N'-di-sec-butyl-p-phenylenediamine showed no cracks after a 2-yr outdoor exposure at 20% elongation. Within the GR-S family, the more ozone-susceptible low-styrene copolymers are the easiest to inhibit by amines. Higher levels of inhibitor are required in the higher styrene copolymers. The presence of 2-3 parts of a conventional antioxidant such as phenyl-2-naphthylamine increases the effectiveness of amine-type antioxidants.

The two main effects of heat deterioration are cross-linking and chain scission. Cross-linking predominates at 158 F and results in hardening and stiffening; chain scission predominates at 212 F and results in softening. GR-S is more prone to cross-linking; natural rubber is more prone to chain scission. Some saturated polymers such as polyacrylates and silicones are very heat-resistant, but others such as Butyl and Thiokol show flow or creep in high-temperature service. Heat-aging is not necessarily linked to oxidation but occurs also in vacuo or in inert atmospheres. Elongation changes offer a more suitable criterion of aging than tensile strength tests. Compositions of superior age-resistance can be obtained by using low-sulfur compounds as accelerators in preference to elemental sulfur.

The role of oxygen in peroxides in GR-S aging seems to be similar to that of sulfur in causing continued cross-linking.

Three oxidation stages—initial, constant-rate, and autocatalytic—can be differentiated. Most physical properties deteriorate beyond usefulness before the end of the constant-rate stage. Typical

synthetic and natural rubber compositions aged both indoors and outdoors for 5 yr lost 10-40% of their original tensile strength and elongation. This loss was equivalent to oven aging for 24-168 hr at 158 F or 24-72 hr at 212 F. Oxygen-aging of polymers protected by antioxidants is not considered to be as severe as that caused by ozone or heat. The amount of oxygen absorbed is not indicative of age resistance, because it does not correlate with physical-property changes.

A-1286

U.S. Arsenal, Rock Island, Ill. Laboratory.
ANTIOXIDANTS FOR GR-S RUBBER, by W.J. Touhey.
Report No. 53-2824. July 1953.

The antioxidant properties of seven commercial and fifteen experimental compounds, of twenty-four waxes, and of their combinations in GR-S 1505 (41-F 90/10 butadiene-styrene) rubber were determined by accelerated tests in the ASTM-D-1149-51T ozone cabinet and in the Firestone Weathering Unit, both at 25 ± 5 ppm ozone at 100 F, and by outdoor exposure at a 45° angle facing south.

Antioxidants that fail in a short time in the ozone cabinet may give good protection to GR-S rubber outdoors because the rate of migration of the antioxidant to the surface of the vulcanizate may be too slow for the high artificial ozone concentration (25 ppm) but fast enough for normal atmospheric ozone concentrations (0 to 9 ppm).

Good ozone protection was obtained with both commercial and experimental amine antioxidants. The most effective compounds were p-phenylenediamine and its N,N-di-sec-butyl (Tenamene II) and N,N'-diphenyl (JZF) derivatives; benzidine and its N,N'-di-sec-butyl derivative; the N,N'-di-sec-butyl derivatives of p-terphenylenediamine and of 1,4-naphthalenediamine; and 4,4'-methylenedianiline (Tonox). Of these compounds, benzidine, N,N'-di-sec-butylbenzidine, Tenamene II, and Tonox gave good protection both in the ozone cabinet and outdoors. There was a definite synergism when a combination of antioxidants was used with Tenamene II. The addition of 1 part wax, to aid migration, enhanced the protective capacity of all antioxidants. Compounds of high vapor pressure did not give good ozone protection to GR-S aged at 158 and 212 F in a circulating-air oven.

A-1287

U.S. Arsenal, Rock Island, Ill. Laboratory.
PRESERVATION OF TIRES IN OUTDOOR STORAGE, by W.J. Touhey.
Report No. 53-2504. May 1953.

The protection of tires on outdoor storage by ozone-resistant coatings, weather-resistant veneers, covers, chemical inhibitors, and waxes was investigated by determining the physical properties and surface condition of GR-S test pads after various aging times in different geographical locations, both with and without protective coatings and with and without chemical inhibitors and waxes.

Presently used preservative coatings for use on mounted tires are unsatisfactory because of their high cost of application and because they are subject to embrittlement, peeling, and rupture when the

vehicle is moved. Similarly, covers for mounted tires are undesirable because of high application cost and because complete sealing is difficult. Heat-sealed covers on unmounted tires may, however, be of some value if the tires are to be stacked one on another in open storage.

Excessive brittleness of MIL-B-12121A strippable vinyl coating after 3-6 mo outdoor exposure is caused by loss of plasticizer, both to the air and into the rubber. When applied at a minimum thickness of 15 mil, preferably 25-30 mil, this coating does not harm GR-S rubber after 1-yr outdoor exposure and does prevent ozone cracks. A 4-mil thickness of MIL-C-11520 Neoprene AC coating protects GR-S rubber from ozone and is flexible after 1-yr outdoors. However, neither MIL-B-12121A nor MIL-C-11520 coatings prevent the natural aging of GR-S rubber, which takes place even in the absence of oxygen.

Ozone-resistant veneers of neoprene or Hypalon S-2 vulcanized to the tire are suitable from a cost standpoint. The ideal method of preservation of Ordnance tires is the incorporation of ozone inhibitors, such as N,N'-di-sec-butyl-p-phenylenediamine (Tenamene II), in the latex during manufacture. The value of most chemical inhibitors is greatly increased when 1% of wax is added as a migration aid.

A-1334

U.S. Naval Shipyard, Brooklyn, N.Y. Material Laboratory.
REPORT OF INVESTIGATION OF PLASTIC TAPE VS. METAL CASTING REPLICA
TECHNIQUES FOR EVALUATION OF OZONE CRACKING OF ELASTOMERIC
MATERIALS, by R. Steinmetz and A.D. Delman.
Lab. Project 4912-5 (Final Report). October 1953.

A-1347

U.S. Arsenal, Rock Island, Ill. Laboratory.
EVALUATION OF NEOPRENE-GR-S RUBBER BLENDS, by Paul M. Rogers.
Report No. 53-2405. July 1953.

Various blends of neoprene Type WRT or Type FR with GR-S (x600) were prepared and evaluated in an effort to obtain rubbers which combine good low-temperature flexibility with improved resistance to weathering, ozone, heat-oven aging, flame, oil, and cut growth.

Blends of 60 parts neoprene WRT or FR with 20 parts GR-S met the oil-swelling limit of 110% specified for the 60-durometer SC grade of MIL-R-3065, and showed fair aging, ozone, flame, and cold resistance. A high-dielectric compound conforming to Spec. AXS1059 (75 neoprene WRT, 25 GR-S 1023) showed slightly greater volume swell in oils than permitted for the SC grade of Spec. MIL-R-3065, but its good low-temperature properties, high dielectric breakdown strength, and good compression set seem to merit its use in special applications.

As the GR-S content of WRT blends was increased there was a gradual decrease in tensile strength and an increase in compression set after 22 hr at 125 F. At the same time, a definite improvement in low-temperature properties was obtained, as indicated by the failure of 60/40 blends and the passing of 70/30 blends subjected

to the ASTM D746 low-temperature brittleness test. Little difference was noted in the ozone resistance of 100/0, 90/10, 80/20, and 70/30 blends of Neoprene WRT/GR-S, but higher GR-S contents caused a rapid decrease in ozone resistance. All Neoprene FR/GR-S blends exhibited poor ozone resistance, but blends containing only 10 parts of GR-S passed the ASTM low-temperature test.

A-1358

U.S. Wright Air Development Center.
SYNTHETIC RUBBERS FROM CARBON-FLUORINE COMPOUNDS, by F.A. Bovey.
Technical Report 52-197, Part 3. September 1953.

The aim of this research was the development of fluorine-containing synthetic rubbers resistant to swelling in fuels, lubricants, and hydraulic fluids and having satisfactory properties at temperatures from -65 F to +350 F.

Properly compounded perfluorobutadiene copolymers show excellent high-temperature properties. Copolymers with 1,1-dihydroperfluoroalkyl(butyl and hexyl) vinyl ethers, in particular, offer excellent heat resistance, low swelling in aircraft fluids, and high ozone resistance. When properly stabilized, they suffer only about 8% weight loss and slight stiffening after 500 hr at 390 F. Copolymers with ethylene are inferior and cannot be prepared in good yields.

Fluoroacrylates, particularly the γ -(perfluoroalkoxy)-1,1-dihydroperfluoropropyl acrylates show an outstanding balance of low-temperature flexibility and resistance to aircraft fluids. Four homopolymers of this series, viz., those in which the alkoxy group is methoxy, ethoxy, propoxy, and butoxy, exhibit a 25-C improvement in low-temperature flexibility over the corresponding 1,1-dihydroperfluoroalkyl acrylates. The homopolymer of γ -(perfluoromethoxy)-1,1-dihydroperfluoropropyl acrylate (FMFPA) shows a Gehman T_{10} temperature of -32 C and swells relatively little in aircraft fluids. A butadiene copolymer of this acrylate, vulcanized in a gum stock, exhibits a Gehman T_{10} value of about -46 C and swells about 60% in both 30% aromatic fuel and in benzene. This compound represents the closest approach to the original requirements for solvent resistance and low-temperature flexibility.

Compounding and vulcanization studies on fluoroacrylate homopolymers led to the development of polyamine curing recipes having greatly improved stability at temperatures as high as 350 F in contact with diester lubricants and other aircraft fluids, improved compression-set properties, and greatly improved resistance to nitric acid and to alkali.

A-1358(2)

U.S. Wright Air Development Center. Directorate of Research.
Materials Laboratory.
SYNTHETIC RUBBERS FROM CARBON-FLUORINE COMPOUNDS, by W.H. Pearlson and N.W. Taylor.
Technical Report 52-197, Part 1. October 1952.

A-1377

U.S. Naval Shipyard, Brooklyn, N.Y. Material Laboratory.
REPORT OF INVESTIGATION OF REPLICA TECHNIQUES FOR EVALUATION OF
OZONE-DETERIORATION OF RUBBER AND SYNTHETIC RUBBER, by
A.D. Delman and R. Steinmetz.
Lab. Project 4912-4 (Final Report). August 1953.

A-1495

U.S. Naval Supply Activities, N.Y. Clothing Supply Office,
Brooklyn, N.Y.
SHELF LIFE OF NEOPRENE COATED NYLON FABRICS, by R. Briganti.
Project NTO01-008, Cold and Wet Weather Clothing Report 2.
April 1955.

After 1-4 1/2 yr storage, eighteen nylon fabrics coated on one side with one of four types of nylon exhibited little or no change in waterproofness, flexibility, breaking strength, weather resistance, and ability to withstand laundering and dry cleaning. There were small losses in tear strength. All four types of neoprene coatings appeared to behave equally well. A Buna-N coated nylon showed moderate loss in tear strength.

The nylon base fabrics, all designed for cold weather clothing, included oxford, twill, plain weave, taffeta, and mesh fabrics. The types of neoprene tested were Neoprene GN, a sulfur-modified chloroprene polymer stabilized by a thiuram disulfide; Neoprene GRT, similar to type GN but containing a nondiscoloring antioxidant, with improved resistance to low-temperature crystallization; Neoprene W, a stabilized chloroprene polymer containing no sulfur or sulfur compounds; and Neoprene WRT, similar in both composition and properties to Neoprene W, but with greater resistance to low temperature crystallization.

From these results, the conclusion is reached that nylon fabrics coated on one side with properly formulated neoprene compounds will have a shelf life of at least 3 yr and probably considerably longer.

A-1519

U.S. Naval Shipyard, Mare Island, Calif. Rubber Laboratory.
EFFECT OF EXPOSURE TO WEATHER AT POINT BARROW, PUGET SOUND, AND
MARE ISLAND ON HARDNESS AND COLD COMPRESSION SET OF GR-S,
NATURAL RUBBER, AND NEOPRENE VULCANIZATES, by A.E. Barrett.
Report No. 69-40. July 1953.

Results of 2-yr exposure tests at Point Barrow, Alaska, Puget Sound, and Mare Island, indicate that vulcanized GR-S soft gasket stocks are more suitable for service in the arctic than are natural rubber or neoprene stocks.

The thirty nine GR-S stocks, which varied only in type of plasticizer, differed among themselves in low-temperature resistance. Volatility and water extractability of the plasticizers were important factors in weather-aging resistance. Di-N-hexyl adipate was an outstanding plasticizer for this service. Of the two natural rubber stocks tested, the normal sulfur stock was somewhat better than a low-sulfur (0.75 parts) stock). Of the three neoprene compounds, Neoprene GN and RT were somewhat better than Neoprene W. Weather aging in arctic climates had less effect on low-temperature properties than did weathering in temperate climates.

At monthly intervals, the hardness of each of the unstrained specimens and the ambient temperature were noted. After exposure, the specimens were returned to the laboratory and Rex hardness at temperatures from -40 to 82 F and compression sets at -35 F were determined and compared with corresponding values obtained before exposure.

PDC Comment: An earlier report from the same source along similar lines has been abstracted by this Center: [A COMPARISON OF THE LOW-TEMPERATURE BEHAVIOR AND PHYSICAL PROPERTIES OF GUAYULE, HEVEA AND GR-S VULCANIZATES. Report 15-8. March 1950, PDA 8:PLAS 187, A-955]

A-1590

U.S. Office of Naval Research.
JOINT ARMY-NAVY-AIR FORCE CONFERENCE ON ELASTOMER RESEARCH AND DEVELOPMENT.

Symposium Report ACR-4, Vol. 2. January 1956.

The Proceedings of the Fourth Joint Army-Navy-Air Force Conference on Elastomer Research and Development is being issued in two parts, of which the present volume is the second. It contains the prepared technical papers received before the Conference. Volume 1 will contain the opening remarks, discussion from the floor, and additional technical papers.

The present volume has been partially abstracted by the Center and includes, in addition, the following subjects: (1) Developmental work on high-temperature polymers in three broad areas, namely fluoro compounds, silicones and inorganic materials; (2) Development of compounds for use at high temperatures in contact with diester lubricants and the effect of such lubricants on existing elastomers; (3) Applications of various elastomers including polyurethane rubber in coatings and flexible foams and latex-dispersed acrylate elastomers cast as dilaminar films for prosthetic use; (4) Testing procedures for dynamic mechanical properties of rubber, stress relaxation versus sealability of gasket materials, and water extractability and migration of plasticizers.

A-1600

Zeitlin, Robert J.
ACCELERATED AND OUTDOOR WEATHERING OF RUBBER.
U.S. Signal Corps. Engineering Laboratories, Fort Monmouth, N.J.
Technical Memorandum 1679. September 1955.

A-1648

U.S. Dept. of the Air Force.
HANDBOOK: INSPECTION, MAINTENANCE, STORAGE, AND DISPOSITION OF AIRCRAFT TIRE CASINGS AND INNER TUBES.
T.O. 4T-1-3. October 1955.

A-1669

U.S. Naval Shipyard, Mare Island, Calif. Rubber Laboratory.
TEST FOR EVALUATING THE TENDENCY OF SYNTHETIC RUBBER GASKET MATERIALS TO LOSE PLASTICIZERS BY VOLATILIZATION, by J. Oser.
Report No. 167-3. August 1953.

A-1676

U.S. Office of Naval Research.
JOINT ARMY-NAVY-AIR FORCE CONFERENCE ON ELASTOMER RESEARCH AND
DEVELOPMENT, THE PENTAGON, JANUARY 11-12, 1956.
Symposium Report ACR-4, Vol. 1. 1956.

A-1777

U.S. Engineer Center, Fort Belvoir, Va. Engineer Research and
Development Laboratories.
RESISTANCE OF RUBBER COVERED CABLE, JACKET, AND INSULATION STOCKS
TO WEATHER AND ARTIFICIAL AGING, by J.W. Bryden, F. Rupert,
M. Smith, and P. Mitton.
Presented at the 5th Annual Symposium on Technical Progress in
Communication Wire and Cables, December, 1956, Asbury Park, N.J.
31 p.

Unstressed GR-S rubber compounded with 4 parts of sunproof wax
showed practically no cracking after 2 yr outdoor exposure. The
low temperature properties of military cables were practically
unchanged after exposure to desert conditions. A general correlation
between tensile strength retention after exposure and weather
cracking was observed.

Materials tested were in the form of cables and sheets and
included GR-S, natural rubber, butyl rubber, and neoprene. Outdoor
weathering tests were conducted on both stressed and unstressed
specimens at Fort Churchill, Fort Belvoir, and Yuma. The effects
of two methods of accelerated weathering were investigated. In
one, stressed and unstressed sheets (6 by 2 by 0.08 in.) were
exposed for 100 and 200 hr in an Atlas Type WX Weatherometer with
filters removed to permit circulation of ozone around the specimens.
Similar sheets were exposed in a Crabtree-Kemp ozone chamber at a
temperature of 100 F at 25 and 50 pphm ozone for 100 hr.

The weatherometer caused significant weathering of several cable
materials, but the results differed markedly from those obtained in
outdoor exposure. This test was considered unsuitable. Although
correlation of ozone chamber results with outdoor weathering data
was limited, this was considered a more satisfactory device for
predicting weather resistance. With ozone concentrations of 50 pphm,
exposure for 100 hr was not adequate to distinguish clearly the
weathering properties of the various materials. Conditioning times
of 150 to 200 hr would be more desirable.

B-498

Gt. Brit. Royal Aircraft Establishment, Farnborough.
STRESS-RELAXATION OF SYNTHETIC RUBBER SHEET MATERIALS IN AIR AND
OZONE, by A. Baker and R.B. King.
Technical Note No. Chem. 1124. April 1950.

Stress decay in strained synthetic rubber sheet materials was
found to be greater in ozonized air at 20 C than in the normal
atmosphere, and revealed the effect of ozone on rubber that was not
visibly cracked. Appreciable stress-relaxation caused by ozone
occurred in 2 days in Neoprene GN protected by a wax film. This
effect was increased in the absence of wax. Perbunan and Hycar
were drastically affected.

A specification test method for grading resistance to ozone is proposed in which the stress-relaxation of the rubber under examination in ozonized air is compared with that of a standard waxed Neoprene GN. The method replaces a previous one which was inapplicable to waxed Neoprene. In the new procedure three tensile test specimens of specified size are cut from both the test and the standard material. The stress required to increase the stem length of each sample 20% in 1 min is measured. The samples are then mounted in an apparatus in such a way as to maintain this elongation and are then exposed to ozonized air flowing at 40-60 liters per min for a total period of 6 hr at 15-25 C. The exposure may be continuous or intermittent. The elongation of the sample is maintained for 48 hr and the stress required to maintain that degree of elongation is measured. For each sample this stress is expressed as a percentage of the originally measured stress. The arithmetic mean of the percentage stress of the three samples is calculated. The ozonized air must contain sufficient ozone to produce a mean percentage stress of 50-60% in the standard rubber material.

C-802(11)

Interchemical Corporation, New York, N.Y. Research Laboratories.
DEVELOPMENT AND FORMULATION OF LOW TEMPERATURE POLYISOBUTYLENE
(BUTYL) RUBBER COMPOUNDS.

Final Report; U.S. Dept. of the Army. Signal Corps. Contract
No. W36-039sc-35580, January 1, 1948 - February 28, 1951.
March 1951.

C-829(18)

United States Rubber Company. Bristol Plant, Bristol, R.I.
INSULATING AND JACKETING COMPOUNDS FOR CABLES USED UNDER
EXTREME CLIMATIC CONDITIONS, submitted by W.H. Dibble and
K.M. Webb.

Final Report; U.S. Dept. of the Army. Signal Corps. Contract
No. W 36-039-sc-36832. November 1949.

Developmental work on thermosetting and thermoplastic synthetic insulating and jacketing compounds for cables operating at ambient temperatures of -55 to +75 C is summarized.

Thermosetting synthetics

Two insulating compounds and one jacket compound made from arctic GR-S polymers containing 90% butadiene and 10% styrene cured at 41 F were developed and used on samples of five types of cable with reasonable satisfactory results. Many butyl insulating compounds were mixed and tested without achieving a serviceable formulation which could be processed. Neoprene jacketing compounds which met specification requirements were developed but were too soft for satisfactory processing.

Requirements specified for thermosetting insulating and jacketing compounds were: (1) tensile strength - 600 psi for types A and B, 700 psi for type E, and 1500 psi for types J and M; (2) elongation - 250% for the first two and 300% for the remaining types; (3) ultimate dielectric strength - minimum 350 v per mil; (4) insulation resistance on cables - K not less than 2000 at 16 C; (5) power factor at 50 C - 2% for type B and 1.5% for type E insulation after 1 day

in water. All compounds were to withstand aging tests, e.g., a 7-day oxygen bomb test at 80 C and 300 psi, and low temperature tests at -55 C of (1) flexural strength by bending around a specified mandrel, (2) brittleness by ASTM methods D-736 or D-746, (3) impact resistance, (4) stiffness by ASTM methods D-747 or D-797, and (5) torsion modulus by a proposed ASTM test method using a modification of the Clash and Berg apparatus.

Insulation type A is for low voltage cords and power cables; type B for microphone cables requiring a low dielectric constant and power factor with good stability after prolonged immersion in water; and type E for Cable RG-28/U which requires dimensional stability conforming with Specification JAN-C-17, high ozone resistance, low dielectric constant and power factor, and excellent stability after prolonged immersion in water. Jacket type J is for cords and cables; and type M for RG-28/U cable which requires dimensional stability, conforming with JAN-C-17, and high ozone resistance. Suitable or promising formulations for each type insulation and jacket are given.

Thermoplastic synthetics

To develop a noncontaminating type L jacket for use over a polyethylene insulated cable, the most promising start was made from a Perbunan - Vinylite compound USR-2418 (C-9-14) with an attempt to eliminate contaminating ingredients and substitute materials which would provide adequate low temperature properties. Jacket compounds developed showed brittle points of -40 to -60 C, adequate tensile strength, elongation, and aging properties, and a power factor increase of 0.5 - 12 times after aging 14 days at 100 C based on tests run at 3000 megacycles on the MIT Co-Ax equipment.

PDC Comment: Details of compounding and testing techniques were given in the regularly issued progress reports that preceded this summarized account; all of these are on file at the Center.
[Progress Reports 1 - 17, May 1948 - August 1949. C-829(1-17)]

C-944(12)

United States Rubber Company. Bristol Plant, Bristol, R.I.
INSULATING AND JACKETING COMPOUNDS FOR CABLES USED UNDER EXTREME CLIMATIC CONDITIONS, FINAL REPORT, by W.H. Dibble, P.C. Jillson, C.P. McKenna, and K.M. Webb.
Report No. 12; U.S. Dept. of the Army. Signal Corps. Contract No. DA 36-039 sc-43, March 20, 1950 through July 20, 1951. July 1951.

Various types of insulating and jacketing compounds for cables were developed mainly from arctic GR-S (butadiene-styrene) polymers. The formulations have satisfactory mechanical, electrical, and chemical properties, and are suitable for operation at ambient temperatures ranging from -55 to +75 C. These formulations include a low voltage type insulation for cords and power cables; a low voltage, low loss insulation for use in microphone cables; a low voltage, extra flexible insulation for use in miniature cables for headsets, handsets, microphones, and receivers; a high voltage, low loss, ozone resistant butyl insulation; a general purpose jacket for cords and cables; and an ozone resistant jacket for use in RG-28U cable.

The lowest temperature at which the butyl compound met all specification requirements was only -45 C. A neoprene jacket was formulated which could be used over the butyl insulation. A Buna N-polyvinyl chloride jacket compound was also developed for use on Spiral Four Cable.

Compositions and properties of the various experimental formulations are included.

PDC Comment: Details pertaining to the development and testing of these insulating compounds can also be found in preceding reports of this project which are on file at the Center.
[Progress Reports 1-11, May 1950 - June 1951; C-944 (1-11)]

C-977

Koppers Company, Inc., Pittsburgh, Pa. Chemical Division.
DI-TERT-BUTYL-PARA-CRESOL (DBPC).
Technical Bulletin No. C-0-115. June 1950.

C-999(14)

Kellogg (M.W.) Company. Petroleum and Chemical Research Dept.
Laboratory Division, Jersey City, N.J.
ARCTIC RUBBER, by F.J. Honn and J.M. Hoyt.
Report RL-54-333; U.S. Quartermaster Corps. Contract DA-44-109-qm-222,
July 1950 - July 1953, Final Summary Report. August 1954.

C-999(16)

Kellogg (M.W.) Company. Petroleum and Chemical Research Dept.
Laboratory Division, Jersey City, N.J.
ARCTIC RUBBER, by A.N. Bolstad.
Report RL-54-367; U.S. Quartermaster Corps. Contract DA-44-109-qm-1580,
April to July, 1954. December 1954.

C-1044(1)

Interchemical Corporation, New York, N.Y. Research Laboratories.
RESEARCH INVESTIGATIONS LEADING TO THE DEVELOPMENT OF IMPROVED
BUTYL RUBBER COMPOUNDS.
Quarterly Report No. 1; U.S. Dept. of the Army. Signal Corps.
Contract No. DA36-039sc 5436. June 1951.

C-1044(8)

Interchemical Corporation, New York, N.Y. Research Laboratories.
RESEARCH INVESTIGATIONS LEADING TO THE DEVELOPMENT OF IMPROVED
BUTYL RUBBER COMPOUNDS.
Final Report; U.S. Dept. of the Army. Signal Corps.
Contract No. DA36-039sc 5436, March 1, 1951 - January 31, 1953.
March 1953.

Investigations during this contract period established the suitability of properly compounded butyl rubber polymers such as GR-I-25 insulating materials for high voltage, ignition, and pulse cables and as semiconduction pulse cable insulation. When precaution is taken to avoid contamination, GR-I-25 can be processed as easily as other conventional elastomers. Its relatively high isoprene content insures a satisfactory rate of cure. Insulating compounds

made with it not only have excellent dielectric properties, but also outstanding impermeability to gases and water vapor, chemical and thermal stability, and resistance to crystallization at low temperatures.

The demand for extreme ozone and corona resistance in pulse ignition cables, however, necessitated the substitution of low isoprene content polymer, such as GR-I-R21, although this is slower curing and much more susceptible to crystallization at low temperatures than is GR-I-25.

A fourfold acceleration of the quinoid cure of GR-I-R21 was obtained using manganese dioxide and benzothiazyl disulfide. This cure also resulted in a rubber compound of higher modulus and lower set.

The incorporation of supplemental polymers such as 20% or more of Hypalon S-2 improved ozone resistance but was detrimental to both electrical and low-temperature properties. Experimental polymers containing small amounts of divinylbenzene and other crosslinking modifiers were intermediate in ozone resistance between GR-I-25 and GR-I-R21 and possessed outstanding resistance to crystallization at low temperatures. Increasing the unsaturation of the compounded polymers reduced the rate of crystallization but was detrimental to ozone resistance.

The use of plasticizers and low filler loadings with GR-I-R21 slightly reduced the crystallization rate but did not remedy the polymer's susceptibility to crystallization at -40 C.

Of the many plasticizers evaluated, sebacate and phosphate esters, amyl naphthalenes, alkylated diphenyl oxides, and Solvaloid L were compatible with butyl rubber and capable of improving low-temperature flexibility. Amyl naphthalenes were superior electrically, and alkylated diphenyl oxides were superior after the compounds had been heat-aged. All plasticizers, however, showed high volatility and none of them were permanent when the compound was subjected to temperatures of 150 C or higher for 24 hr or longer. Some slight improvement in both low-temperature flexibility and plasticizer retention was obtained by blending the plasticizer in a 2:1 ratio with raw butyl polymer at 200 C for periods up to 72 hr and then incorporating this blend into the rubber compound. A Kenflex plasticized butyl compound can safely be used as jacketing for polyethylene or other high dielectric materials without fearing excessive dielectric contamination.

Of the many fillers evaluated, silicas and silicates such as Hi-Sil and Silene EF were most effective in smoothing out the extrusion. They stiffened the rubber compound at low temperatures, however, and were harmful to electrical properties. Ferric oxides provided excellent reinforcement and gave compounds with superior low-temperature flexibility but did not smooth out the extrusion and were also harmful electrically. Pure and hydrated aluminum oxides, and Whitetex and Iceberg clays were intermediate in their effect on smoothness and yielded compounds with excellent electrical properties. Blends of aluminum oxides and clay are, therefore, recommended as fillers where extreme smoothness is not required. Where a smoother extrusion is required, the addition of a silica will be of help. In general, total filler in the amount of 100 to 150 parts per 100 of rubber hydrocarbon was most satisfactory for extrusion compounds.

Small quantities of absorptive carbon black—1 part or less per 100 of rubber hydrocarbon—lowered the power factor at 3000 megacycles and

increased the insulation resistance. More than 5 parts of equally dispersed black were invariably harmful to all dielectric properties and also affected the mechanical and low-temperature properties.

Butyl rubber compounds must be properly compounded, processed, and cured to realize their full potential. Of special importance to the corona resistance of the insulation compound is that it be vulcanized in high-pressure steam and that it be cooled under pressure subsequent to cure to eliminate porosity. The semiconducting compound must be prepared according to modifications which produce minimum dispersion of the black, by adding it at the very end of the mixing cycle on a loose, two-roll mill and stopping the milling operation as soon as all of the black has been incorporated. Relatively large percentages of plasticizers should be used to reduce the shear strength of the compound and the dispersion of the black both on the mill and in the extruder.

Satisfactory semiconduction butyl rubber compounds for pulse cable application comprise, per 100 parts GR-I-R21, 50-60 parts acetylene black, 15 alkylated diphenyl oxide, 5 zinc oxide, 2.5 sulfur, and 1 part each of thiuram disulfide and tellurium dithiocarbamate.

PDC Comment: More detailed information on this contract project can be found in earlier progress reports on file at the Center. [Quarterly Reports 1-7, June 1951 - November 1952; PDC C-1044(1-7)]

C-1051

du Pont de Nemours (E.I.) and Company, Wilmington, Del.

Rubber Chemicals Division.

EFFECT OF COMPOUNDING ON OZONE RESISTANCE OF NEOPRENE VULCANIZATES. Bulletin BL-238. September 1950.

The inherently good ozone resistance of neoprene vulcanizates can be further improved for severe service by proper compounding. Stocks prepared with such softeners as coal tar derivatives, mineral rubber, factice, or coumarone-indene resins possess high permanent set and low modulus, and thus promote ozone resistance by relieving stress. Low states of cure and mineral fillers function in a similar manner but such compounding has limited application.

When only static stress is involved, from 2 to 5 parts of a hydrocarbon wax such as Heliozone can be used. This shields the elastomer from ozone by forming a wax bloom. A suitable antioxidant is beneficial for all applications in which either static or dynamic stress is involved; in dynamic operations antioxidants offer the most practical method of protection. Akroflex C and F are markedly beneficial for this purpose. Neozones in quantities ranging from 3 to 5 parts are also effective. Certain nondiscoloring antioxidants are detrimental.

Most conventional plasticizers intensify the cracking of neoprene vulcanizates in ozone; low-temperature plasticizers are particularly detrimental especially if used to the extent of 15 pph neoprene. Process oils having petroleum bases are also harmful. Poor dispersion of fillers, flow cracks, pebbling, and other imperfections in the finished part also decrease ozone resistance. Neoprene Type W is slightly more resistant to ozone than other types of neoprene.

C-1153 United States Rubber Company. Naugatuck Chemical Division,
Naugatuck, Conn.
FLEXAMINE, A SUPERFLEXING ANTIOXIDANT.
Compounding Research Report No. 15. [n.d.] 9 p.

C-1161 Dow Corning Corporation, Midland, Mich.
DOW CORNING 4 COMPOUND, PROPERTIES AND APPLICATIONS IN THE
ELECTRICAL POWER AND OTHER INDUSTRIES.
Silicone Notes 4-201. December 1952.

C-1204 Firestone Tire and Rubber Company, Akron, Ohio.
AGING OF NATURAL AND SYNTHETIC RUBBERS, FINAL REPORT.
Ordinance Contract No. DA-33-019-ORD-723. February 1953.

Measuring the changes in physical properties is still the best means of following the aging of GR-S vulcanizates. Ultimate elongation and modulus are particularly sensitive parameters of aging. Data correlating the decay of physical properties in GR-S stock and the useful service life of tires are, however, still lacking.

Oxygen absorption studies appear inadequate for measuring the aged condition of rubber stocks, mainly because of the effect of elevated temperatures on physical properties and because it is difficult to correlate these properties with oxygen uptake. Similarly, in accelerated aging studies at elevated temperatures, the rapid stiffening of GR-S black stocks, which is almost independent of oxygen uptake, must be considered.

Although there is no real correlation between the oxygen and antioxidant contents and the physical properties of samples aged at elevated temperatures, the antioxidant disappearance during natural aging can be taken as a means of estimating the progress of aging if the original antioxidant concentration is known and if an accurate analytical method for determining the antioxidant content of aged samples can be worked out.

A combination of amine and phenolic type antioxidants and waxes was found to offer the best protection to both Hevea and GR-S black-loaded rubber stocks, particularly for prolonged storage under static strained conditions.

PDC Comment: The aging behavior of regular GR-S, cold GR-S, and natural rubber, and the influence of carbon black on aging properties are described in the following report on file at the Center.
[U.S. Arsenal, Rock Island, Ill. Laboratory (John E. Maurer).
FIVE YEAR SUMMARY OF THE FIRE-STONE-CASE AGING CONTRACT,
Report 53-2371. June 1953; PDC A-1244]

C-1234(20)

Burke Research Company, Van Dyke, Mich.
DEVELOPMENT OF OZONE AND/OR OXYGEN RESISTANT POLYMERS, by R.G. Spain.
Final Technical Report and Report No. 20; U.S. Ordnance Corps.
Contract No. DA-20-089-ORD-36531, June 1, 1952 to February 28, 1954.
February/March 1954.

The problem of imparting ozone resistance to tire stocks was approached by modifying GR-S polymer compounds with additives and by developing new elastomers with superior inherent ozone resistance. Resistance under dynamic conditions was emphasized and an apparatus was designed to continuously elongate and relax specimens 30 times per min during ozone exposure. Static exposure tests at Detroit, Miami, and Pasadena provided data on combined ozone and oxidation resistance. Control samples were made from an ozone-resistant GR-S formulation containing 1.5 parts wax and 2 parts of Santoflex AW, a commercially available antioxidant.

Of the new elastomers tested, pyridine-type monomers had higher dynamic ozone resistance without the use of antioxidants, than the GR-S controls. An outstanding compound was Hypalon S-2 (a chloro-sulfonated polyethylene) in 50/50 blends with GR-S 1500.

GR-S compounds containing 2.5 to 5.0 parts of several additives had 10 times greater ozone resistance when tested dynamically and even greater resistance when tested in laboratory ozone cabinets and at weathering stations than the control compound. These additives are described only as a series of structurally similar compounds prepared by the Universal Oil Products Company and by the Burke Research Company. Heat aging of rubber containing these experimental antioxidants had no serious effect on ozone resistance.

In general, ozone attack appears to be minor for elastomers with low amounts of chemically unsaturated bonds, e.g., butyl rubber, Hypalon S-2, and diisocyanate-polyester compositions. Oil or wax surface film formations do not protect GR-S compounds against ozone attack in either dynamic or weather tests. The ability to migrate to the surface of the rubber, however, appears to be characteristic of effective antioxidants since a surface bloom appears on such protected compounds. This migration may be essential for preventing crack initiation after the surface antioxidant is depleted.

Additives which reportedly decompose ozone and hydroperoxide into oxygen, and water plus oxygen, respectively, do not protect GR-S rubber against ozone. Nor do unsaturated or olefinic additives which should preferentially react with ozone. The usual types of antioxidants, which should be readily oxidized by ozone, do not show high ozone resistance, even in higher than usual loadings. Protection against ozone appears to be given by specific types of additives which are not necessarily oxidized directly by ozone. Some of the effective compounds react with air at room temperature whereas others do not.

Results of this study are in disagreement with the theory that an antioxidant terminates free-radical chain reactions initiated by reaction of ozone with unsaturated bonds of elastomers.

PDC Comment: Detailed information on this project is available in several earlier progress reports dated August 1952 through February 1954. These reports are also on file at the Center under the catalogue numbers C-1234(1-8,16-19).

- C-1304 Denman Rubber Manufacturing Company, Warren, Ohio.
DEVELOPMENT OF OZONE AND/OR OXYGEN RESISTANT POLYMERS.
Technical Reports 1, 2, and 3; U.S. Ordnance Corps.
Contract DA-20-089-ORD-36580, Final Report. June 1953 -
April 1954.
- C-1444 United States Steel Corporation. American Steel and Wire Division,
Cleveland, Ohio.
[TO DEVELOP AN OZONE RESISTANT BUNA-N JACKET COMPOUND WHICH WILL
MEET THE LOW TEMPERATURE AND FUNGUS RESISTANT REQUIREMENTS
OF MIL-C-13486 AND WILL CONFORM AS CLOSELY AS POSSIBLE TO ALL
OTHER REQUIREMENTS OF MIL-C-13486; TO ADJUST THIS COMPOUND TO
BE A PRACTICAL FACTORY COMPOUND, AND TO PRODUCE A SAMPLE
LENGTH OF CABLE UTILIZING THIS COMPOUND], signed: R.H. Haberstroh
and W.G. Dahlstrom.
U.S. Ordnance Corps. Contract DA-33-019-ORD-1741, Report 1.
June 1955.
- C-1445 United States Steel Corporation. American Steel and Wire Division,
Cleveland, Ohio.
[TO DEVELOP AN OZONE RESISTANT BUNA-N JACKET COMPOUND WHICH WILL
MEET THE LOW TEMPERATURE AND FUNGUS RESISTANT REQUIREMENTS OF
MIL-C-13486, AND WILL CONFORM AS CLOSELY AS POSSIBLE TO ALL
OTHER REQUIREMENTS OF MIL-C-13486; TO ADJUST THIS COMPOUND TO
BE A PRACTICAL FACTORY COMPOUND, AND TO PRODUCE A SAMPLE LENGTH
OF CABLE UTILIZING THIS COMPOUND], signed: R.H. Haberstroh and
W.G. Dahlstrom.
U.S. Ordnance Corps. Contract DA-33-019-ORD-1741, Report 4.
December 1955.
- C-1446 United States Steel Corporation. American Steel and Wire Division,
Cleveland, Ohio.
[TO DEVELOP AN OZONE RESISTANT BUNA-N JACKET COMPOUND WHICH WILL
MEET THE LOW TEMPERATURE AND FUNGUS RESISTANT REQUIREMENTS OF
MIL-C-13486, AND WILL CONFORM AS CLOSELY AS POSSIBLE TO ALL
OTHER REQUIREMENTS OF MIL-C-13486; TO ADJUST THIS COMPOUND TO
BE A PRACTICAL FACTORY COMPOUND, AND TO PRODUCE A SAMPLE LENGTH
OF CABLE UTILIZING THIS COMPOUND], signed: R.H. Haberstroh and
W.G. Dahlstrom.
U.S. Ordnance Corps. Contract DA-33-019-ORD-1741, Report 3.
October 1955.
- C-1447 United States Steel Corporation. American Steel and Wire Division,
Cleveland, Ohio.
[TO DEVELOP AN OZONE RESISTANT BUNA-N JACKET COMPOUND WHICH WILL
MEET THE LOW TEMPERATURE AND FUNGUS RESISTANT REQUIREMENTS OF
MIL-C-13486, AND WILL CONFORM AS CLOSELY AS POSSIBLE TO ALL
OTHER REQUIREMENTS OF MIL-C-13486; TO ADJUST THIS COMPOUND TO BE
A PRACTICAL FACTORY COMPOUND, AND TO PRODUCE A SAMPLE LENGTH OF
CABLE UTILIZING THIS COMPOUND], signed: R.H. Haberstroh and
W.G. Dahlstrom.
U.S. Ordnance Corps. Contract DA-33-019-ORD-1741, Report 2.
August 1955.

C-1459 Cooper Tire and Rubber Company, Findlay, Ohio.
DEVELOPMENT OF WEATHER AND AGING RESISTANT PNEUMATIC TIRES.
U.S. Ordnance Corps. Contract DA-20-089-ORD-36588, Final Technical
Report. June 1954.

C-1482 Burke Research Company, Van Dyke, Mich.
DEVELOPMENT OF PRACTICAL ANTIOZONANTS, by F.C. Bruce.
U.S. Ordnance Corps. Contract DA-20-089-ORD-36531, Report No. 41.
March 1956.

C-1494 Burke Research Company, Van Dyke, Mich.
DEVELOPMENT OF PRACTICAL ANTIOZONANTS, by R.G. Spain.
U.S. Ordnance Corps. Contract DA-20-089-ORD-36531, Report No. 30.
April 1955.

C-1495 Burke Research Company, Van Dyke, Mich.
DEVELOPMENT OF PRACTICAL ANTIOZONANTS, by R.G. Spain.
U.S. Ordnance Corps. Contract DA-20-089-ORD-36531, Report No. 31.
May 1955.

C-1497 Burke Research Company, Van Dyke, Mich.
DEVELOPMENT OF PRACTICAL ANTIOZONANTS, by R.G. Spain.
U.S. Ordnance Corps. Contract DA-20-089-ORD-36531, Report No. 33.
July 1955.

C-1498 Burke Research Company, Van Dyke, Mich.
DEVELOPMENT OF PRACTICAL ANTIOZONANTS, by R.G. Spain.
U.S. Ordnance Corps. Contract DA-20-089-ORD-36531, Report No. 34.
August 1955.

C-1499 Burke Research Company, Van Dyke, Mich.
DEVELOPMENT OF PRACTICAL ANTIOZONANTS, by R.G. Spain.
U.S. Ordnance Corps. Contract DA-20-089-ORD-36531, Report No. 35.
September 1955.

C-1500 Burke Research Company, Van Dyke, Mich.
DEVELOPMENT OF PRACTICAL ANTIOZONANTS, by R.G. Spain.
U.S. Ordnance Corps. Contract DA-20-089-ORD-36531, Report No. 38.
December 1955.

C-1501 Burke Research Company, Van Dyke, Mich.
DEVELOPMENT OF PRACTICAL ANTIOZONANTS, by R.G. Spain.
U.S. Ordnance Corps. Contract DA-20-089-ORD-36531, Report No. 40.
February 1956.

- C-1513 Dayton Rubber Company, Dayton, Ohio.
[TO DETERMINE THROUGH AN ENGINEERING STUDY THE FEASIBILITY OF
USING BUTYL RUBBER IN MECHANICAL ITEMS.]
U.S. Ordnance Corps. Contract DA-33-008-ORD-1071, Report No. 3.
August 1955.
- C-1514 Dayton Rubber Company, Dayton, Ohio.
[TO DETERMINE THROUGH AN ENGINEERING STUDY THE FEASIBILITY OF
USING BUTYL RUBBER IN MECHANICAL ITEMS.]
U.S. Ordnance Corps. Contract DA-33-008-ORD-1071, Report No. 4.
October 1955.
- C-1515 Cooper Tire and Rubber Company, Findlay, Ohio.
DEVELOPMENT OF WEATHER AND AGING RESISTANT PNEUMATIC TIRES.
U.S. Ordnance Corps. Contract DA-20-089-ORD-36588, Final Technical
Report. June 1954.
- C-1541 United States Steel Corporation. American Steel and Wire Division,
Cleveland, Ohio.
[TO DEVELOP AN OZONE RESISTANT BUNA-N JACKET COMPOUND WHICH WILL
MEET THE LOW TEMPERATURE AND FUNGUS RESISTANT REQUIREMENTS OF
MIL-C-13486, AND WILL CONFORM AS CLOSELY AS POSSIBLE TO ALL
OTHER REQUIREMENTS OF MIL-C-13486; TO ADJUST THIS COMPOUND TO
BE A PRACTICAL FACTORY COMPOUND, AND TO PRODUCE A SAMPLE LENGTH
OF CABLE UTILIZING THIS COMPOUND], signed: R.H. Haberstroh and
W.G. Dahlstrom.
U.S. Ordnance Corps. Contract DA-33-019-ORD-1741, Report 5.
February 1956.
- C-1542 United States Steel Corporation. American Steel and Wire Division,
Cleveland, Ohio.
[TO DEVELOP AN OZONE RESISTANT BUNA-N JACKET COMPOUND WHICH WILL
MEET THE LOW TEMPERATURE AND FUNGUS RESISTANT REQUIREMENTS OF
MIL-C-13486, AND WILL CONFORM AS CLOSELY AS POSSIBLE TO ALL
OTHER REQUIREMENTS OF MIL-C-13486; TO ADJUST THIS COMPOUND TO
BE A PRACTICAL FACTORY COMPOUND, AND TO PRODUCE A SAMPLE LENGTH
OF CABLE UTILIZING THIS COMPOUND], signed: R.H. Haberstroh and
W.G. Dahlstrom.
U.S. Ordnance Corps. Contract DA-33-019-ORD-1741, Report 6.
April 1956.
- C-1551 Dayton Rubber Company, Dayton, Ohio.
PROPOSED METHOD OF APPROACH TO THE PREVENTION OR MINIMIZING OF OZONE
ATTACK ON TIRES AND MECHANICAL GOODS.
U.S. Ordnance Corps. Contract DA-20-089-ORD-36756, Report 1.
January 1954.

- C-1552 Dayton Rubber Company, Dayton, Ohio.
[DEVELOPMENT OF OZONE RESISTANT GR-S COMPOUNDS SUITABLE FOR USE
IN PNEUMATIC TIRES AND MECHANICAL GOODS.]
U.S. Ordnance Corps. Contract DA-20-089-ORD-36756, Report 2.
January 1954.
- C-1553 Dayton Rubber Company, Dayton, Ohio.
[DEVELOPMENT OF OZONE RESISTANT GR-S COMPOUNDS SUITABLE FOR USE
IN PNEUMATIC TIRES AND MECHANICAL GOODS.]
U.S. Ordnance Corps. Contract DA-20-089-ORD-36756, Report 3.
February 1954.
- C-1554 Dayton Rubber Company, Dayton, Ohio.
[DEVELOPMENT OF OZONE RESISTANT GR-S COMPOUNDS SUITABLE FOR USE
IN PNEUMATIC TIRES AND MECHANICAL GOODS.]
U.S. Ordnance Corps. Contract DA-20-089-ORD-36756, Report 4.
March 1954.
- C-1555 Dayton Rubber Company, Dayton, Ohio.
[DEVELOPMENT OF OZONE RESISTANT GR-S COMPOUNDS SUITABLE FOR USE
IN PNEUMATIC TIRES AND MECHANICAL GOODS.]
U.S. Ordnance Corps. Contract DA-20-089-ORD-36756, Report 5.
[n.d.]
- C-1556 Dayton Rubber Company, Dayton, Ohio.
[DEVELOPMENT OF OZONE RESISTANT GR-S COMPOUNDS SUITABLE FOR USE
IN PNEUMATIC TIRES AND MECHANICAL GOODS.]
U.S. Ordnance Corps. Contract DA-20-089-ORD-36756, Report 6. [n.d.]
- C-1557 Dayton Rubber Company, Dayton, Ohio.
[DEVELOPMENT OF OZONE RESISTANT GR-S COMPOUNDS SUITABLE FOR USE IN
PNEUMATIC TIRES AND MECHANICAL GOODS.]
U.S. Ordnance Corps. Contract DA-20-089-ORD-36756, Report 7. [n.d.]
- C-1558 Dayton Rubber Company, Dayton, Ohio.
[DEVELOPMENT OF OZONE RESISTANT GR-S COMPOUNDS SUITABLE FOR USE IN
PNEUMATIC TIRES AND MECHANICAL GOODS.]
U.S. Ordnance Corps. Contract DA-20-089-ORD-36756, Report 8. [n.d.]
- C-1559 Dayton Rubber Company, Dayton, Ohio.
[DEVELOPMENT OF OZONE RESISTANT GR-S COMPOUNDS SUITABLE FOR USE IN
PNEUMATIC TIRES AND MECHANICAL GOODS.]
U.S. Ordnance Corps. Contract DA-20-089-ORD-36756, Report 9. [n.d.]
- C-1560 Dayton Rubber Company, Dayton, Ohio.
[DEVELOPMENT OF OZONE RESISTANT GR-S COMPOUNDS SUITABLE FOR USE IN
PNEUMATIC TIRES AND MECHANICAL GOODS.]
U.S. Ordnance Corps. Contract DA-20-089-ORD-36756, Report 10. [n.d.]

- C-1561 Dayton Rubber Company, Dayton, Ohio.
[DEVELOPMENT OF OZONE RESISTANT GR-S COMPOUNDS SUITABLE FOR USE IN
PNEUMATIC TIRES AND MECHANICAL GOODS.]
U.S. Ordnance Corps. Contract DA-20-089-ORD-36756, Report 14.
January 1955.
- C-1562 Dayton Rubber Company, Dayton, Ohio.
[DEVELOPMENT OF OZONE RESISTANT GR-S COMPOUNDS SUITABLE FOR USE IN
PNEUMATIC TIRES AND MECHANICAL GOODS.]
U.S. Ordnance Corps. Contract DA-20-089-ORD-36756, Report 15.
February 1955.
- C-1563 Dayton Rubber Company, Dayton, Ohio.
[DEVELOPMENT OF OZONE RESISTANT GR-S COMPOUNDS SUITABLE FOR USE IN
PNEUMATIC TIRES AND MECHANICAL GOODS.]
U.S. Ordnance Corps. Contract DA-20-089-ORD-36756, Report 17.
April 1955.
- C-1564 Dayton Rubber Company, Dayton, Ohio.
[DEVELOPMENT OF OZONE RESISTANT GR-S COMPOUNDS SUITABLE FOR USE IN
PNEUMATIC TIRES AND MECHANICAL GOODS.]
U.S. Ordnance Corps. Contract DA-20-089-ORD-36756, Report 20.
July 1955.
- C-1565 Dayton Rubber Company, Dayton, Ohio.
[DEVELOPMENT OF OZONE RESISTANT GR-S COMPOUNDS SUITABLE FOR USE IN
PNEUMATIC TIRES AND MECHANICAL GOODS.]
U.S. Ordnance Corps. Contract DA-20-089-ORD-36756, Report 22.
September 1955.
- C-1566 Dayton Rubber Company, Dayton, Ohio.
[DEVELOPMENT OF OZONE RESISTANT GP-S COMPOUNDS SUITABLE FOR USE IN
PNEUMATIC TIRES AND MECHANICAL GOODS.]
U.S. Ordnance Corps. Contract DA-20-089-ORD-36756, Report 23.
October 1955.
- C-1567 Dayton Rubber Company, Dayton, Ohio.
[DEVELOPMENT OF OZONE RESISTANT GR-S COMPOUNDS SUITABLE FOR USE IN
PNEUMATIC TIRES AND MECHANICAL GOODS.]
U.S. Ordnance Corps. Contract DA-20-089-ORD-36756, Report 24.
November 1955.
- C-1568 Dayton Rubber Company, Dayton, Ohio.
[DEVELOPMENT OF OZONE RESISTANT GR-S COMPOUNDS SUITABLE FOR USE IN
PNEUMATIC TIRES AND MECHANICAL GOODS.]
U.S. Ordnance Corps. Contract DA-20-089-ORD-36756, Report 25.
December 1955.

C-1574

Dayton Rubber Company, Dayton, Ohio.
AN ENGINEERING STUDY TO DETERMINE THE FEASIBILITY OF USING BUTYL
SYNTHETIC ELASTOMER IN MECHANICAL RUBBER ITEMS, by D.A. Meyer
and J.G. Sommer.
U.S. Ordnance Corps. Contract DA-33-008-ORD-1071, Final Technical
Report. December 1955.

Butyl rubber was successfully compounded to meet the low-temperature and brittleness requirements for mechanical rubber goods such as wheel and master cylinder boots and air brake and windshield wiper hose. High levels of plasticizers were required with the most effective compounds being also the most fugitive. The plasticizers which varied widely in effectiveness included 2-butoxyethanol pelargonate, 2-(2-butoxyethoxy)ethanol pelargonate, trioctyl phosphate, white oil, diisooctyl adipate, diisooctyl sebacate, dibutyl sebacate, and tris(2-ethylhexyl) phosphate. Vulcanizates containing diisooctyl sebacate had outstanding plasticizer retention properties.

All of the plasticizers lowered the ozone resistance of the compounds to a level below that normally associated with butyl rubber. Reduced ozone resistance was particularly severe at the higher plasticizer levels. To overcome this deficiency, various antiozonants were tested, with and without wax. One of these (composition unspecified) used in conjunction with 1 part wax enhanced the ozone resistance more than thirtyfold and was chosen for use in the end items.

C-1585

Burke Research Company, Van Dyke, Mich.
DEVELOPMENT OF PRACTICAL ANTIOZONANTS, by F.C. Bruce.
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[EFFECT OF OZONE ON RUBBER DETERIORATION], MONTHLY PROGRESS REPORT
FOR JANUARY 1955, by R.E. Thompson.
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- C-1601 Lee Rubber and Tire Corporation, Conshohocken, Pa.
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- C-1602 Lee Rubber and Tire Corporation, Conshohocken, Pa.
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FOR MAY 1955, by R.E. Thompson.
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June 1955.
- C-1605 Lee Rubber and Tire Corporation, Conshohocken, Pa.
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1955.

C-1616 Wetmore Hodges and Associates, Inc. Detroit Arsenal Test Operation,
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 OZONE RESISTANT COMPONENTS.
 Project MB-127, Progress Report No. 5, Contract DA-04-200-ORD-370.
 1955.

C-1617 Wetmore Hodges and Associates, Inc. Detroit Arsenal Test Operation,
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 OZONE RESISTANT COMPONENTS.
 Project MB-127, Progress Report No. 6, Contract DA-04-200-ORD-370.
 1955.

C-1618 Wetmore Hodges and Associates, Inc. Detroit Arsenal Test Operation,
 Camp Bullis, Tex.
 OZONE RESISTANT COMPONENTS.
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 1955.

C-1619 Wetmore Hodges and Associates, Inc. Detroit Arsenal Test Operation,
 Camp Bullis, Tex.
 OZONE RESISTANT COMPONENTS.
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 Project MB-127, Progress Report No. 9, Contract DA-04-200-ORD-370.
 1955.

C-1621 Wetmore Hodges and Associates, Inc. Detroit Arsenal Test Operation,
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 OZONE RESISTANT COMPONENTS.
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 1955.

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 1955.

C-1623 Wetmore Hodges and Associates, Inc. Detroit Arsenal Test Operation,
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 OZONE RESISTANT COMPONENTS.
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 1955.

- C-1624 Wetmore Hodges and Associates, Inc. Detroit Arsenal Test Operation,
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 OZONE RESISTANT COMPONENTS.
 Project MB-127, Progress Report No. 13, Contract DA-04-200-ORD-370.
 1955.
- C-1625 Wetmore Hodges and Associates, Inc. Detroit Arsenal Test Operation,
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 OZONE RESISTANT COMPONENTS.
 Project MB-127, Progress Report No. 14, Contract DA-04-200-ORD-370.
 1955.
- C-1626 Wetmore Hodges and Associates, Inc. Detroit Arsenal Test Operation,
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 OZONE RESISTANT COMPONENTS.
 Project MB-127, Progress Report No. 15, Contract DA-04-200-ORD-370.
 1955.
- C-1627 Wetmore Hodges and Associates, Inc. Detroit Arsenal Test Operation,
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 1955.
- C-1628 Wetmore Hodges and Associates, Inc. Detroit Arsenal Test Operation,
 Camp Bullis, Tex.
 OZONE RESISTANT COMPONENTS.
 Project MB-127, Progress Report No. 17, Contract DA-04-200-ORD-370.
 1955.
- C-1629 Wetmore Hodges and Associates, Inc. Detroit Arsenal Test Operation,
 Camp Bullis, Tex.
 OZONE RESISTANT COMPONENTS.
 Project MB-127, Progress Report No. 18, Contract DA-04-200-ORD-370.
 1955.
- C-1630 Wetmore Hodges and Associates, Inc. Detroit Arsenal Test Operation,
 Camp Bullis, Tex.
 OZONE RESISTANT COMPONENTS.
 Project MB-127, Progress Report No. 19, Contract DA-04-200-ORD-370.
 1955.
- C-1631 Wetmore Hodges and Associates, Inc. Detroit Arsenal Test Operation,
 Camp Bullis, Tex.
 OZONE RESISTANT COMPONENTS.
 Project MB-127, Progress Report No. 20, Contract DA-04-200-ORD-370.
 1955.

- C-1632 Wetmore Hodges and Associates, Inc. Detroit Arsenal Test Operation,
Camp Bullis, Tex.
OZONE RESISTANT COMPONENTS.
Project MB-127, Progress Report No. 21, Contract DA-04-200-ORD-370.
1955.
- C-1633 Wetmore Hodges and Associates, Inc. Detroit Arsenal Test Operation,
Camp Bullis, Tex.
OZONE RESISTANT COMPONENTS.
Project MBR-127, Progress Report No. 22, Contract DA-04-200-ORD-370.
1955.
- C-1634 Wetmore Hodges and Associates, Inc. Detroit Arsenal Test Operation,
Camp Bullis, Tex.
OZONE RESISTANT COMPONENTS.
Project MBR-127, Progress Report No. 23, Contract DA-04-200-ORD-370.
1955.
- C-1635 Wetmore Hodges and Associates, Inc. Detroit Arsenal Test Operation,
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OZONE RESISTANT COMPONENTS.
Project MBR-127, Progress Report No. 24, Contract DA-04-200-ORD-370.
1955.
- C-1636 Wetmore Hodges and Associates, Inc. Detroit Arsenal Test Operation,
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Project MBR-127, Progress Report No. 25, Contract DA-04-200-ORD-370.
1955.
- C-1637 Wetmore Hodges and Associates, Inc. Detroit Arsenal Test Operation,
Camp Bullis, Tex.
OZONE RESISTANT COMPONENTS.
Project MBR-127, Progress Report No. 26, Contract DA-04-200-ORD-370.
1956.
- C-1644 Mansfield Tire and Rubber Company, Mansfield, Ohio.
DEVELOPMENT OF WEATHER AND AGEING RESISTANT PNEUMATIC TIRES.
U.S. Ordnance Corps. Contract DA-20-089-ORD-36637, Final Report.
November 1953.
- C-1658 Wetmore Hodges and Associates, Inc. Detroit Arsenal Test Operation,
Camp Bullis, Tex.
OZONE RESISTANT COMPONENTS.
Project MBR-148, Progress Report No. 1, Contract DA-04-200-ORD-370.
1956.

G-381

Hum, J.K.Y. and M.B. Leggett.
EFFECT ON COPPER NAPHTHENATE IN FABRICS ON THE AGING OF RUBBER.
Chemical Warfare Service Development Laboratory, Massachusetts
Institute of Technology. September 8, 1945. 36 p.

Test sheets of 65% natural rubber, reclaimed rubber, Neoprene, GR-S, Buna N, and GR-I were aged in the presence of fabric containing 0.9% of copper as copper naphthenate, with and without lubricating oil added. These materials were aged in a Geer Oven and in tropical and desert storage rooms. The rubber was not deteriorated when no oil was present. When oil was added to the fabric, the copper accelerated the damage only when the oil itself had an effect on the rubber. It is recommended that copper naphthenate be considered as a permissible fungicide for gas mask carriers.

G-763

Fuller, C.S.
SOME RECENT CONTRIBUTIONS TO SYNTHETIC RUBBER RESEARCH.
Bell System Tech. J. 25:351-384. July 1946.

This article gives a short account of the history of synthetic rubber research and the theories underlying the behavior of polymers, paying particular attention to the solution of problems which arose during the war in the development of GR-S, a copolymer of butadiene and styrene. Scientific methods for measuring and controlling important characteristics of rubber polymers are discussed. Some of these characteristics are (1) the over-all or average styrene content in the butadiene-styrene copolymer, (2) the percentage of soap, fatty acids, and low molecular butadiene-styrene compounds in the rubber, (3) the amount of gel fraction, if present, and the swelling volume of the gel, (4) the average molecular size of the sol fraction of the copolymer, (5) the degree of branching of the sol molecules, and (6) the molecular weight distribution of the sol.

PDC Comment: Other reviews of recent developments in the rubber industry include the following:

- (1) Boss, A.E. and Richard W. KixMiller.
Rubber developments in 1945. Chem. Eng. News 24:336-338. 1946.
- (2) Bourdon-Michelin, Pierre.
Discovery and scientific research in the rubber industry.
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- (3) Chilton, E.G.
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- (4) Colin, G.
The rubber industry in Japan. I. The development and the importance of the Japanese rubber industry up to the opening of hostilities with China. Rev. gén. caoutchouc 21:59-62. 1944. II. The war economy. Ibid. 104-106.
- (5) de Broglie, Louis.
Scientific research and technical research.
Rev. gén. caoutchouc 20:45-49. 1943.

- (6) Demongeot, Alfred.
Natural rubber and synthetic rubber in the U.S.S.R.
Rev. gén. caoutchouc 20:213-214. 1943.
- (7) Hunter, J.S.
New synthetic rubbers. Ind. Fibres, Synthetics, and
By-Products 7:231-232. 1945.
- (8) Weidlein, E.R., Jr.
Synthetic rubber research in Germany. Chem. Eng. News
24:771-774. 1946.
- (9) Wilson, Robert S.
Rubber today and tomorrow. Natl. Engr. 50:32-35. 1946.

G-764

Clark, Frederick E. and Wilfred E.L. Place.
EVALUATION OF BLENDS OF GUAYULE AND GR-S RUBBERS.
Ind. Eng. Chem. 38:1026-1033. October 1946.

The following natural rubbers were blended with GR-S, all-purpose synthetic rubber, in various proportions, and the resultant tread stock samples were tested for physical properties: Hevea smoked sheet from Honduras, latex guayule from 3-yr-old cultivated shrub, alkali-alcohol treated guayule from mature Mexican shrub, guayule from retted 3-yr-old cultivated shrub, resinous guayule from 3-yr-old cultivated shrub, and resinous guayule from mature Mexican wild shrub.

Although some properties, such as abrasion resistance, suffered, a considerable overall improvement was noted when up to 20% of any of the natural rubbers was compounded with GR-S. The lower-resin guayule rubbers and Hevea smoked sheet improved the physical properties of GR-S vulcanizates more than did the higher-resin guayules, whereas the latter produced more improvement in processing characteristics and tack.

The authors recommend that in blending synthetic rubber with even a small amount of natural rubber, their practice of adjusting the formulas to meet the compounding requirements of each rubber in the blend be followed, since an enormous difference in physical characteristics can be noted with different formulas.

PDC Comment: The British Advisory Service on Plastics and Rubber reported that, as regards dynamic stiffness, a 50/50 natural-rubber/GR-S mixture compared favorably with pure natural rubber, whereas 100% GR-S was not satisfactory [Advisory Service on Plastics and Rubber. Progress Report, July 1944. - Supp. 1:32, B-50].

G-1052

Battelle Memorial Institute, Columbus, Ohio.
LITERATURE SURVEY ON AGING AND STORAGE OF VULCANIZED RUBBER GOODS;
ARTILLERY STORAGE PROGRAM.
U.S. Army. Ordnance Dept. Contract W33-019-ORD-5333. May 1946.

One hundred eighty references are cited in this summary of the literature dealing with problems of long term storage of vulcanized rubber and its products.

According to the majority of opinions given in the literature, ideal conditions for 2 - 5 yr storage of rubber are: Temperature

of 10 - 20°C, static nitrogen atmosphere, maximum humidity, and total darkness. The goods are to be in an unstressed condition and metal contacts should be avoided. Oil, grease, and dirt should be removed with soap and water prior to storage.

Crude rubber can be stored satisfactorily over long periods, but vulcanized rubber continues to cure upon aging. Storage in a damp atmosphere is the best protection against oxidation, which is the reaction most damaging to rubber.

A wide variety of chemicals and mixtures have been recommended for use as surface preservatives.

It is generally agreed that air, light, heat, and oil speed the deterioration of rubber. Storage in vacuo or in inert gases, total immersion, as in water, and the use of gas absorbents and solid dehydrating agents have all been recommended. Carbon dioxide is the most generally preferred inert gas. Absorbents such as oxides of lead or slaked lime, placed out of contact with the rubber, should be present to remove such gases as hydrogen sulfide, hydrogen chloride, or oxygen which may diffuse from the surface of the stored material.

Correlation of accelerated tests with natural aging, is also considered.

G-1119

Crabtree, James and A.R. Kemp.

ACCELERATED OZONE WEATHERING TEST FOR RUBBER.

Ind. Eng. Chem. (Anal. Ed.) 18:769-774. December 1946.

An accelerated test for evaluating susceptibility of rubber to atmospheric ozone cracking is discussed and an apparatus for conducting the test and for measuring ozone in minute concentration is described in detail.

It has been previously established by the authors that two separate and distinct factors contribute to the deterioration of rubber outdoors: A light-energized oxidation and an ozone attack. The former acts independently of stress in the rubber, the latter only when the material is stretched. The integral deterioration in any particular time depends on the relative intensities of these two factors.

The test atmosphere consisted of 25 ± 2 parts by volume of ozone per 100,000,000 of air. The measure of performance was the expiration of time for the first appearance of cracks in the stressed sample at the chosen degrees of elongation (usually 20 and 30%) and temperature. The test temperature selected for a given type of compound is such that the economically practicable addition of protective wax can be made to fail in 3 or 4 days. For natural rubber 70 - 80 and 110 F and for GR-S rubber 120 - 125 F are suggested temperatures.

Ozone is furnished by passing air or oxygen over a mercury vapor lamp having an envelope of quartz or glass transmitting short-wave ultraviolet light. Since ozone is very unstable, a rapid method of estimation had to be devised in order to assure a uniform concentration. The amount of ozone was determined by absorbing it in a solution of potassium iodide in water and estimating the iodine liberated by titrating with thiosulfate using a galvanometer.

A large volume of air must be used to furnish sufficient iodine for measurement in the short time allotted. The air to be measured was made to generate a fine spray of potassium iodide solution, thus furnishing an enormous surface of solution for the reaction.

Titration must not be conducted in bright daylight and during the ozone run the whole absorption apparatus must be enclosed in a light-tight box, since potassium iodide in solution is photochemically oxidized to iodine in the presence of light even in neutral or alkaline solution. Correction must be made for the iodine carried away in the exhausted air.

Comparative data on natural and GR-S vulcanizates are given with particular reference to the effect of different proportions of protective wax.

G-1273

Zane, Robert B.

SYNTHETICS AS USED IN WIRES AND CABLES.

Okonite Company, Passaic, N.J. Research Laboratory Publication 108-A.
September 1945.

G-1479

Fielding, J.H.

EXPOSURE CRACKING OF RUBBER.

Indian Rubber World 115:802-805. March 1947.

Goodyear has conducted a series of tests on tire compounds of natural rubber which help to explain anomalies encountered in service and discrepancies between roof aging and tire performance. Wax is included in weather-resisting rubber in excess of its solubility so that it will migrate to the surface and form a protective film. The tests show that under conditions in which this film remains intact it protects stretched rubber from the cracking and checking caused by exposure. If the film is broken or is entirely removed, the rubber may be more severely affected by exposure than if it had contained no wax.

The new testing methods developed in this research are:

(1) Static outdoor exposure

Tapered strips of rubber were mounted on racks facing the sun in such a way as to be stretched 10 - 22% and to have free air circulation on all sides. Wax stocks were superior to nonwax stocks in resistance to checking. Under static conditions the wax film was undisturbed and evidently was effective in protecting the rubber.

(2) Dynamic outdoor exposure

Strips were mounted as in (1) except that one end of each strip was attached to an oscillating drum. The stretch of the rubber was varied from 0 to 10 - 22%. This was in no sense a fatigue test. Under dynamic conditions the film is broken purely by relative motion of adjacent parts of the surface. The nonwax stocks were definitely superior. Some of the wax-containing compounds, however, were better than others and almost equal to the nonwax stocks.

(3) Ozone exposure with unbroken film

Specimens were mounted in stretched position, heated to dissolve existing film, and aged 3 days to allow a uniform film to develop. They were then exposed to ozone for 30 min, since it is fairly well established that all exposure cracking of stretched rubber is due to ozone. The results of this test correspond to those of static outdoor exposure and confirm the superiority of wax-containing rubbers under conditions favorable to maintenance of the film.

(4) Ozone exposure with films removed

The rubber was washed with acetone, stretched while wet, washed again, and exposed to ozone after about 5 min drying. Two of the wax stocks were in worse condition than the nonwax stocks, as was the case with the dynamic outdoor exposure, indicating that the wax content is harmful under these conditions. The third wax stock was no worse than the nonwax compounds, which points to the possibility of overcoming the difficulty by suitable formulations.

G-1651

Borders, A.M., R.D. Juve, and L.D. Hess.
STYRENE-DIENE RESINS IN RUBBER COMPOUNDING.
Ind. Eng. Chem. 38:955-958. September 1946.

A new copolymer, Pliolite S-3, composed of approximately 15 parts butadiene and 85 parts styrene may be used in many Pliolite applications, often with distinct advantages over either natural or synthetic rubber derivatives. This thermoplastic has excellent oxygen and chemical resistance and is compatible with natural rubber and with most synthetic rubbers. In mixtures with rubber as a reinforcing resin, it is valuable for improvement of smoothness during extrusion or calendering and for reduction of shrinkage. Although Pliolite S-3 alone is brittle at room temperatures, in mixtures with rubber up to 50 parts of each, it does not increase the rate at which the mixture stiffens with reduction in temperature. Data are tabulated which illustrate the effect of the 15 butadiene-85 styrene copolymer in GR-S or natural rubber compounds upon hardness, stiffness, extrudability, tensile strength, and impact resistance.

Because of its processing characteristics, dielectric properties, and low moisture absorption, this copolymer has found applications in wire insulation. It is also useful as a stiffening and reinforcing agent in rubber and synthetic rubber footwear. When blended in certain proportions with synthetic rubbers, Pliolite S-3 has unique balata like properties, and has been used to replace costly balata for certain articles such as golf ball covers.

G-1925

Gehman, S.D., D.E. Woodford, and C.S. Wilkinson, jr.
LOW TEMPERATURE CHARACTERISTICS OF ELASTOMERS.
Ind. Eng. Chem. 39:1108-1115. September 1947.

A laboratory method for measuring the stiffness of elastomers at low temperatures has been developed. Modulus determinations are made by using a simple and convenient torsion apparatus.

Strips of the stock to be tested are mounted around a cylindrical insulated chamber. The temperature in the chamber is controlled by cooling the base externally with dry ice and by regulating a flow of precooled air through dry ice in the bottom of the chamber. This system gives stable temperatures which are easily controlled. The chamber can be rotated to attach the samples in succession to a suitably mounted torsion wire. The stiffness is measured by the angle of twist of the sample when the torsion head is rotated 180°.

Plots of angle twist against temperature show a rather sharp break at the low temperature end of the curve; the curve rises slowly until the transition region is reached, a sharp rise occurs, and then the curve levels off. If the transition portion of the curve is extrapolated toward the temperature axis, a value of the temperature within one degree of the freezing temperature is obtained. This value is somewhat subjective but appears to be a much more significant criterion for evaluating low temperature properties than does the brittle point unless the service for a rubber compound actually includes the possibility of a low temperature brittle failure.

Curves illustrate the information which may be obtained from this torsion modulus test for low temperature stiffening characteristics.

The stiffness of elastomers which are capable of crystallization upon stretching, such as Hevea, Neoprene, and butyl rubber, depends not only on temperature but also on time of exposure. To study these effects, the same apparatus was used in a room at -30 C. The rubber specimens were subjected to an induction period of 2.5 mo during which time the stiffness is essentially constant. It then increases and eventually reaches a larger constant value. Several months may be required to complete these changes. No change was observed in the stiffness of GR-S which does not crystallize when stretched. X-ray examination of Hevea and butyl rubber proved that the increased stiffness on long exposure was due to crystallization.

Reduction in the speed of retraction is a critical measure of the deterioration of high elasticity at low temperatures. It gives a wide differentiation at moderately low temperatures between butyl rubber and Hevea or GR-S, whereas a slow modulus test does not.

PDC Comment: In a talk on the development of rubber with low temperature flexibility, P.R. Proto of the Chemical Corps Technical Command stated that two tests used by this organization to determine flexibility were adapted from the standard Chemical Corps procedure for coated fabrics. In one test an empirical stiffness coefficient is determined from the successive loadings required to deflect a loop-shaped sample from its original circular shape to maximum deformation. In the second method the stiffness coefficient is determined from a single deflection of the loop. Results obtained by the second procedure are more consistent and reproducible.

[U.S. Joint Army-Navy Deterioration Prevention Committee, Main Committee. MINUTES OF THE ELEVENTH MEETING. 9 p. Oct. 2, 1947. - 3: J 31, A-256(11)]

G-2093

Shelton, J. Reid and Hugh Winn.
OVEN AND BOMB AGING OF GR-S AT CORRESPONDING TEMPERATURES.
Ind. Eng. Chem. 39:1133-1136. September 1947.

The differences observed in the results obtained in oxygen bomb and air oven aging of GR-S rubber cannot be directly correlated. An explanation of the causes of these differences is based on a calculation of activation energies.

The effect of temperature and of oxygen concentration were separately evaluated by comparing the results of both oven and bomb aging at 80 and 100 C. Rectangular strips were cut from tensile sheets and triplicate samples were removed for testing after 1,2,4,6,8, and 10 days at 80 C, and once daily for 5 days at 100 C. A pressure of 300 lb per sq in. was maintained in the oxygen bomb. The tensile strength, elongation at break, and the stress at both 200 and 300% elongation were determined for all samples.

Increased temperature was found to increase the severity of both types of aging; this effect is greater at the higher oxygen concentration in the bomb.

An increase in modulus, largely the result of attack by oxygen, is less in the oxygen bomb than in the air oven at the same temperature. The reaction of oxygen with GR-S is apparently little affected by concentrations of oxygen greater than that in air. The smaller modulus increase is apparently due to a balancing of the effects of cross linkage which causes hardening and chain scission which softens the rubber. The behavior of the modulus curve at both temperatures supports this interpretation of the observations. Tensile breakdown in oxygen bomb aging also indicates chain scission.

Changes in temperature and in oxygen concentration, therefore, alter the ratio of the fundamental aging reactions of chain scission and cross linking. Since the effect of these two reactions upon physical properties is different, no direct correlation can be expected between methods of aging which differ in both temperature and oxygen concentration.

The energy of activation calculated from the temperature coefficients is 29.7 Cal for tensile breakdown in the oxygen bomb and 18.2 Cal for modulus increase in the air oven. These values may be regarded as approximations of the energies required for chain scission and cross linking, respectively. It is possible that, at the temperatures involved, a relatively large number of oxygen molecules are sufficiently activated to maintain the lower energy reaction of cross linking even in air, but few have the energy required for the scission reaction; consequently, the increased oxygen concentration in the bomb will make available a larger number of molecules for the latter reaction. It is also possible that, although both reactions are apparently initiated by oxygen, additional oxygen may be required for chain scission but not for cross linking.

PDC Comment: The following improvements for oven and bomb tests are among those suggested by the Gt. Brit. Advisory Service on Rubber:

- (1) The physical properties of the rubber should be measured at the aging temperature.

- (2) Oven and bomb tests should be conducted at the lowest practical temperature.
- (3) Standard dimensions should be specified for the test pieces.
- (4) Test pieces should be aged in special individual containers.
- (5) At least two physical properties should be measured to follow the progress of oven or bomb aging.
- (6) Elongation at break, in the absence of reversion, is most suitable as a general criterion of oven and bomb aging. Modulus values should be checked for indications of reversion and, if the latter is found, tensile strength is to be preferred to elongation at break a measurement of aging.

[A STUDY OF ACCELERATED AGEING TESTS. 19 p. April 1947. -
4: Plas 40, B-296]

G-2239

Konkle, G.M., R.R. Selfridge, and P.C. Servais.
BEHAVIOR OF SILASTIC ON AGING.
Ind. Eng. Chem. 39:1410-1413. November 1947.

The properties of silicone rubbers on which most commercial uses depend are heat resistance, low temperature flexibility, weather resistance, and oil resistance. The stability of these rubbers was evaluated after exposure to heat, cold, weather, and oil. They were able to withstand conditions which produce temporary or permanent changes in carbon-based elastomers.

The inherent stability of the silicone polymer is emphasized by the fact that special compounding is not necessary to produce stocks resistant to many conditions. Rubber compounds can be altered by an indefinite number of techniques, but no single formulation combines resistance to more than a few of the conditions which usually cause elastomers to deteriorate.

The properties of silicone rubber can also be varied to a certain extent by compounding. Silicone rubber contains a dimethylsiloxane polymer and suitable fillers, and the individual properties of the various stocks are obtained by varying the kind and amount of filler.

The most significant characteristic of a silicone rubber is its retention of properties after exposure to heat. After 50-days heating at 392 F, all Silastic samples tested were still flexible enough to be bent 180° without cracking or breaking; the average weight loss was 6.3% and the shrinkage was 4.0%; the increase in hardness averaged 23 points. At 482 F, the Silastic samples failed the flexing test between 42 and 50 days; the weight loss was 11.0%, the shrinkage 7.1%, and the hardness increased 29 points.

The same Silastic were tested at temperatures from +32 to -100 F for brittleness and hardness change. In the brittleness test, two samples of each stock were exposed to different temperatures for 5 hr and then bent double. The brittle point of Silastic 167 was -80 F, that of Silastic 180 was -90 F, and that of Silastic 181 was -80 F. Evidently the kind of filler has little influence on the brittle points of Silastic stocks, and low temperature flexibility, like the high temperature behavior, is an inherent property of the silicone

rubbers. Flexure at low temperature did not harm the elastomer until the brittle point was reached. Such properties as tensile strength, elongation, and hardness showed no change after return to room temperature.

The rise in hardness, measured on the Shore Durometer, was very gradual as the temperature was lowered to -67 F. Below this temperature the rise was abrupt, and at -76 F all of the formulations showed durometer readings of 90 - 100 points.

There was little variation in the capacity of the various Silastic stocks to resist the effects of a 70-hr immersion in oil at 350 F. The stocks having titanium dioxide as a filler retained their original properties slightly better than did the other stocks. In general, at 350 F silicone rubber swells in oil, but to a lesser extent than do most organic rubbers. It deteriorates only slightly and does not discolor the oil.

Both tensile strength and elongation of Silastic are somewhat reduced by outdoor exposure. Samples, however, which had been held looped for 1 yr out of doors showed no tendency to crack if held under tension. Some strips that were stretched 20% for 1 yr outdoors, likewise did not check or crack.

Both 1-yr outdoor exposure tests and 50-day Weather-Ometer tests indicate that titanium dioxide in the filler of Silastic stocks contributes to the retention of elongation. On the other hand, silicon dioxide contributes to the retention of tensile strength. It seems that the titanium stocks have slightly better over-all weather stability than the silica-filled stocks.

G-2407

Hart, E.J. and M.S. Matheson.
THE QUANTUM YIELD OF OXIDATION OF HEVEA RUBBER AND GR-S.
J. Am. Chem. Soc. 70:784-791. 1948.

The initial low quantum yields of photooxidation obtained for purified Hevea rubber and GR-S suggests that this process is not a chain reaction in its initial stages. Photooxidation apparently involves the addition of molecular oxygen to a light-activated group to form a relatively stable intermediate which does not immediately dissociate to give a free radical reaction chain.

Quantum yields were measured for various mercury-arc lines in the wave length region 2537 - 17,400 A. All experiments were carried out at room temperature and at an oxygen pressure of 1 atm. Data were obtained on initial and 3-hr quantum yields.

It was found that (1) all initial quantum yields are of the order of 1.0 or less, (2) initial and 3-hr quantum yields are lower for GR-S than for rubber, (3) quantum yields for rubber and GR-S decrease with increasing wave length, dropping rapidly above 3660 A for rubber, and above 2800 A for GR-S, and (4) initial efficiencies are lower than the 3-hr yields at 2537 and 3130 A for both polymers, and also at 3660 A for GR-S.

The explanation given for the increase in the 3-hr yield over the initial yield is that the original stable intermediate, presumably a hydroperoxide, eventually attains such a concentration that a small but definite fraction of the light is absorbed by the hydroperoxide. This absorbed light decomposes it into radicals which initiate oxidation chains.

The lack of chain character is especially apparent at longer wave lengths where oxidation is carried to slight extents. The quantum yield remains constant during the entire period of irradiation and exhibits none of the autocatalytic character associated with the usual peroxidation of rubber.

The phenyl group is the light-activated group in GR-S, and it seems likely that the photon energy is not as readily transferred from the benzene nucleus to the adjacent carbon-hydrogen grouping as from the double bond in rubber. Such an effect would explain the lower quantum yields of GR-S compared with rubber.

PDC Comment: This article is an initial investigation of the quantitative fundamentals of the breakdown of rubber and GR-S under the influence of various wavelengths of light. Data of this nature are useful in delineating actual reaction mechanisms occurring in deterioration processes and in ruling out the less likely processes.

Several questions are brought to light and probably will stimulate further work. The article is recommended to anyone interested in the breakdown of rubber and GR-S and, by extension, other high polymers.

Also recommended is Heyroth's revision of Ellis and Wells' book, *THE CHEMICAL ACTION OF ULTRAVIOLET RAYS*; Reinhold Publishing Corp., New York, 1941, 961 p.

G-2477

Bateman, L.
PHOTOLYSIS OF RUBBER.
J. Polymer Sci. 2(1):1-9. 1947.

Rubber hydrocarbon irradiated in vacuo is decomposed by ultraviolet light of wave lengths less than $4000 \text{ \AA}$. The rubber very rapidly becomes insoluble and liberates a gaseous mixture which consists mainly of hydrogen when the irradiation temperature is less than 150 C. The reaction characteristics have been investigated and point to the occurrence of dissociation processes similar to those deduced for comparable simple olefins. When irradiated above 150 C, small but significant amounts of isoprene appear in the volatile product, thereby providing an experimental means of determining the activation energy for separating isoprene from a polyisoprene chain terminated by an allyl radical.

Gas evolution starts immediately upon irradiation and is linearly dependent on the intensity and duration of the irradiation. In less than 0.5 hr of irradiation the rubber becomes insoluble, causing swelling in liquids and a decrease in plasticity. Increased molecular complexity by cross linking is evident. At 200 C isoprene is produced at about $2 \times 10^{-7} \text{ g mol per hr}$.

The rubber specimens used were either intermediate fractions or were obtained by repeatedly fractionating acetone-extracted pale crepe from 85% benzene - 15% methanol solutions in an atmosphere of purified nitrogen. The light source was a Hanovia U-shaped S-250 mercury lamp with reflector, normally placed 12 cm from the rubber. The rubber was maintained at constant temperature by immersing its container in running tapwater. Light intensity was measured with a uranyl oxalate actinometer.

G-2632

Albert, H.E., G.E.P. Smith, jr., and G.W. Gottschalk.
EFFECT OF IRON ON AGING OF GR-S.
Ind. Eng. Chem. 40:482-487. March 1948.

Soluble iron in GR-S polymer was found to accelerate deterioration during oven aging and to increase the rate of oxygen absorption. In contrast to natural rubber, the aging of the raw GR-S polymer was accelerated more by iron than by copper or manganese.

The amount of deterioration caused by a given concentration of iron depended to a large extent on the effectiveness of the anti-oxidant used to protect the polymer. When aluminum sulfate containing low amounts of iron was employed as a coagulant for GR-S latex instead of a grade of higher iron content, the resistance to aging was improved and the rate of oxygen absorption of the GR-S polymer was decreased. On the other hand, a GR-S polymer coagulated by the grade of aluminum sulfate of higher iron content was somewhat more resistant to oven aging and it absorbed oxygen at a slower rate than a polymer coagulated with salt and acid.

The rate of deterioration during artificial aging and the rate of oxygen absorption of GR-S vulcanizates were somewhat increased by polymer-soluble iron, but relatively high concentrations were required to produce much effect. At a concentration at which iron caused slight acceleration of vulcanizate aging, copper or manganese had little or no effect.

G-2737

Painter, E.V.
SOME ASPECTS OF THE AGEING OF COATED FABRICS.
Am. Dyestuff Reprtr. 36:P767-P774. December 1947.

The deterioration of coated fabrics due to aging is determined by (1) the aging resistance of both the fabric and the coating composition and (2) the interaction of the fabric and the film. The latter was shown to be usually the less serious of the two losses, especially for a coated fabric with the film adhering only to one side.

An electronic tensile tester was used to determine the tensile and tear properties of samples of Perbunan SC coated cotton and GR-S coated nylon both before and after aging in an electric oven, in a weatherometer unit, and outdoors. The tensile and also the tear properties of the fabrics, both with and without the coating, were measured by ASTM methods. The energy to rupture or tongue-tear energy was taken to express in a single index the net change due to stiffening or aging. This energy was obtained from the planimetered areas of averaged load-elongation diagrams.

Aging of rubbery materials consists of two opposing mechanisms, viz., (1) cross linking or vulcanization, and (2) rupturing of existing chains and cross links. The first process usually dominates in the initial stages and produces a stronger material; the second becomes appreciable only after the first is completed and has a weakening effect. These factors make themselves evident in tensile test results.

All types of aging produce some shrinking of coated fabrics resulting in an increased elongation at break. When no loss in

strength occurs, this increase in elongation results in an increased energy to rupture. In extreme cases the loss in tensile strength outweighs the shrinkage effect, and the energy decreases. The effect of increased film strength and decreased film extension is referred to as 'elongation balance'. This effect is caused by the fact that the coating and fabric are loaded in parallel and thus each holds a load depending upon the net extension of the parallel system. Before aging, the coating has considerable more extension than the fabric and therefore contributes but little strength at the breaking extension of the fabric. Aging produces a rapid decrease in the extensibility of the coating and a point is reached at which the breaking extension of both fabric and coating are the same, and each contributes its maximum available strength at break. It is thus possible for this balancing effect to produce a net increase in the strength of the combined system even though each member is sustaining a loss from its maximum.

Tongue tear diagrams show that after aging, the drop in tear load from each maximum peak has been greatly diminished and that there is an increase in the number of peaks per unit length. Obviously the stress distribution during tear has been changed by the stiffening of the coating. This is much more marked for the totally impregnated nylon than for the one-side calendered cotton, since in the former the movement of the yarns is restricted, shorter lengths of yarns are extended, and the yarns tend to break one by one rather than as a group.

G-3011

Schulze, W.A., W.B. Reynolds, and C.F. Fryling.
THE MANUFACTURE AND PROPERTIES OF PHILPRENE LOW-TEMPERATURE RUBBER.
India Rubber World 117:739-742. March 1948.

Philprene A and B are low-temperature synthetic rubbers produced by Phillips Petroleum Co. Both are butadiene-styrene copolymers containing approximately 24% bound styrene. The former is manufactured by emulsion polymerization at 5 C and the second at -10 C.

Philprene A preferably contains about 5% disproportionated rosin acid when finished, making it comparable in that respect with GR-S-10. Vulcanizates of the A compound possess high tensile strength at normal and elevated temperatures, great resilience, long flex life, good abrasion resistance, and exceptional processing characteristics.

Philprene B formulations contain fatty acid, disproportionated rosin acid, or mixtures thereof, depending upon requirements. The physical properties of the B compound are generally superior to those of the A, particularly in both treated and carcass recipes at low black loadings.

Results of road tests show that the tread wear of Philprene A tires, containing either channel or furnace black, is 20 - 40% better than that of GR-S-10; this is accompanied by excellent cracking and cut-growth characteristics. Treads reinforced with Philblack O are superior to first line natural rubber treads in both tread wear and cracking characteristics. Extensive road tests have not yet been made on Philprene B.

G-3012

Crabtree, James and A.R. Kemp.
WEATHERING OF SOFT VULCANIZED RUBBER.
Ind. Eng. Chem. 38:278-296. March 1946.

G-3058

Albert, Harry E.
EFFECT OF CERTAIN ANTIOXIDANTS IN GR-S. NATURAL AND ACCELERATED
AGING.
Ind. Eng. Chem. 40:1746-1750. September 1948.

In both natural and oven aging, phenyl-2-naphthylamine gives more protection to GR-s than equal percentages of 2,2,4-trimethyl-6-phenyl-1,2-dihydroxyquinoline, heptylated diphenylamine, or dimethylacridan. A concentration of 1% of the naphthylamine gives maximum protection during both types of aging, only a small amount of this antioxidant being consumed during 5 yr of natural aging. The maximum protective effect with the dihydroxyquinoline is obtained at concentrations of 1.5 - 2%.

After vulcanication the dihydroxyquinoline is slightly more effective than the naphthylamine. The latter, however, gave better protection to a tire-tread type of GR-S vulcanizate against the deleterious catalytic action of a soluble iron compound than did the dihydroxyquinoline. Similar reversals in activity have been found by other workers.

Where comparisons are possible, the results of aging tests of raw and vulcanized GR-S agree well with oxygen-absorption data on these rubbers obtained by other investigators. This is further evidence of the importance of oxygen absorption for evaluating antioxidants in GR-S.

The polymer samples used in this investigation were prepared from uninhibited GR-S latex taken from an autoclave just before the addition of a stopping agent. A commercial grade of the desired antioxidant was added in the form of a dispersion, and the mixture was coagulated with a 2% aluminum sulfate solution. The coagulate was washed on a laboratory mill and dried for 20 hr at 75 C.

Natural aging behavior was observed after 1, 2, and 5 yr at room temperature, in the absence of light, by visual and hand examination and, in the earlier stages of stiffening, by Mooney plasticity determinations. Accelerated aging was carried out at 90 C for 4 days in a forced-circulation air oven. The amount of phenyl-2-naphthylamine in the polymers after natural aging was determined using a Beckman quartz prism spectrophotometer.

G-3244

Harris, Thomas H. and Robert D. Stiehler.
THE AGING OF GR-S; A REVIEW OF THE LITERATURE.
India Rubber World 118:365-366,371-372. June 1948.

G-3335

Reinsmith, Gerald.
AGING AND PRESERVATION OF VULCANIZED RUBBER. I. A STUDY OF FACTORS
AFFECTING AGING DETERIORATION OF VULCANIZED RUBBER, METHODS FOR
EVALUATING AND MEANS OF PRESERVATION.
India Rubber World 117:65-68,74. October 1947.

G-3347

Mayo, L.R., R.S. Griffin, and W.N. Keen.
ACCELERATED AGING OF NEOPRENE COMPOUNDS; EFFECT OF COPPER.
Ind. Eng. Chem. 40:1977-1980. October 1948.

When neoprene containing 1% of an effective antioxidant, such as Neozone D (phenyl-2-naphthylamine), is extruded and cured over a copper conductor, tinning of the wire or use of a special copper inhibitor is necessary only where extremely severe aging conditions prevail. Under these special conditions 1 - 2% of a compound such as the disalicylidenediamines of propylene and ethylene provides an insulation on bare copper equal to that on tinned copper under all conditions.

Neoprene containing 1% copper stearate, used as a contaminant, and no antioxidant deteriorated so rapidly after 5 days in oxygen under 300 psi that no physical tests were possible. The addition of 1% Neozone D resulted in outstanding improvement. Use of a copper inhibitor but no antioxidant was relatively ineffective in retarding degradation in an oxygen-pressure test regardless of the presence or absence of copper stearate. Two parts of the inhibitor in the presence of Neozone D, however, gave full protection against 1.0% of the copper compound.

Accelerated aging tests at 70 C in an air oven for 170 days and in an oxygen bomb for 49 days demonstrated that when extruded directly on copper wire the neoprene containing both antioxidant and 2% copper inhibitor was equal in performance to the vulcanizate without the inhibitor on tinned wire.

Insulation compounds were extruded to a wall thickness of 3/64 in. on base- and tinned-solid copper conductors and cured in a high pressure vulcanizer for 22 sec at a steam pressure of 225 psi. Tensile strength and elongation at break were used as a measure of physical properties.

G-3348

Cosler, V.A. and S.W. McCune, 3rd.
ADVANCES IN RUBBER DURING 1947.
Mech. Eng. 70:307-312. April 1948.

A resumé of the advances made in rubber technology during the year 1947 shows that, even with the increased consumption of natural rubber, a considerable proportion of the research and development efforts of the rubber industry has been directed toward improving the properties of synthetic-rubber products. There has been an increased interest in the testing of rubber products and a noticeable trend toward the experimental evaluation of finished products under simulated service conditions. Thorough determinations of the properties of new polymers and compounds have revealed characteristics in synthetic rubber compositions which make them better suited to certain applications than are products made from natural rubber.

These developments have gone a long way toward overcoming the original prejudice against synthetic rubber products as temporary substitutes and have resulted in their acceptance by users on the basis of their merits.

A bibliography of 195 references is included.

G-3470

Gregory, John B., Irving Pockel, and John F. Stiff.
EFFECT OF STORAGE AND TEMPERATURE ON FLEXIBILITY OF NATURAL AND
SYNTHETIC RUBBERS.
India Rubber World 117:611-616. February 1948.

A new method for measuring the flexibility of rubber consists essentially in determining the stress-strain curve obtained by loading and unloading a loop formed from a 1- by 6-in. strip cut from a test slab. A coefficient of flexibility independent of the thickness of the sample can be obtained together with information on resilience.

Using this method, the behavior of various natural and synthetic rubber gas mask parts was studied during 1 - 3 mo exposure at temperatures down to -20 F. Progressive stiffening probably due to crystallization was found for natural rubber, GR-I, and GR-M compounds at low temperatures. No tendency to crystallize was noted for GR-S. Of the crystallizable polymers, GR-I was the most resistant to stiffening during low-temperature storage and GR-M the least.

The resistance of elastomer compounds to stiffening during prolonged low-temperature storage was found to be improved by (1) using interpolymers made from monomer mixtures having a relatively large proportion of each component, thus obtaining mutual interference with crystallization, and (2) using a 'tight' cure which probably so impedes the movement of the polymer chains that crystallization becomes difficult.

G-3675

Youmans, E.D.
CABLE COVERINGS.
Encyclopedia Chem. Technol. 2:697-716. 1948.

The various properties of the following materials used in insulating and coating electrical wires and cables are reviewed: (1) fibrous substances including asbestos, glass, cotton, jute, rayon, silk, varnished cloth, and paper, (2) rubber including natural rubber, Buna-S (GR-S), Buna-N, butyl rubber, neoprene, thiokol, and silicone rubber, (3) thermoplastics including bitumen and wax compounds, gutta-percha, nylon, polyvinyl-types, polyethylene, and polyisobutylene, (4) varnishes and other coatings including enamels, lacquers, paints, varnishes, and vinyl acetal resin, and (5) metal protective covering including aluminum, copper and copper alloys, lead, monel metal, steel, and zinc.

The types of insulation and protective covering employed are usually determined by the service conditions and cost. Thus, rubber insulation with a bitumen-saturated, cotton-braid covering is used on low-voltage wires and cables in buildings, whereas mineral-oil-impregnated paper covered with an extruded lead sheath is used for high-voltage, underground power cables. The important requirement of adequate flexibility for both insulation and covering eliminates many materials, especially as coverings.

The quality and suitability of cable coverings are tested by various methods, depending on the materials used, the design of the cable, and the service conditions to be encountered. Electrical testing of insulations includes dielectric strength, measured over

the entire useful length, insulation resistance, usually measured on 10 - 15 ft samples, and capacity and power-factor, which may be measured on long or short samples. The most important nonelectrical tests include the following: tensile strength and elongation at break; accelerated aging, usually at elevated temperatures; bending at room and low temperatures; crushing, deformation, and impact resistance; accelerated weathering; water absorption; ozone resistance; flammability; corrosion; and oil and solvent resistance.

G-3697(1)

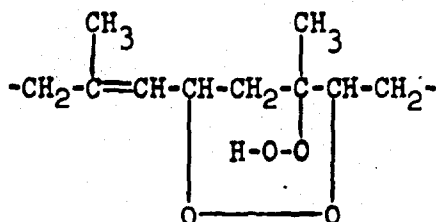
Houwink, R., ed.
ELASTOMERS AND PLASTOMERS: THEIR CHEMISTRY, PHYSICS, AND TECHNOLOGY.
VOLUME 1. GENERAL THEORY.
New York, New York, Elsevier, 1950. 495 p.

G-3729

Cole, John O.
CHEMICAL CHANGES IN ELASTOMERS AND ANTIOXIDANTS DURING AGING.
Presented at Spring Meeting of the American Society for Testing
Materials, March 2, 1949. 12 l.

The present status of knowledge concerning chemical changes occurring in elastomers and antioxidants during thermal or photochemical oxidation is summarized. Recent work indicates that both thermal and photochemical oxidation proceed by the same basic mechanism to form a hydroperoxide as the initial oxidation product.

Investigations of the oxidation of natural rubber show that the initial oxidation product is predominately of the hydroperoxide type. A more complex peroxide similar to the following type may also be formed:



As the reaction proceeds, peroxide decomposition and other secondary reactions lead to the formation of a complex mixture of oxidation products.

The nature of reactions leading to chain scission is not clear. Scission accompanies oxidation even during the early stages. Any possibility of a simple mechanism for the utilization of oxygen in scission reactions seems to be ruled out because of the marked decrease in molecular weight resulting from the absorption of even small quantities of oxygen.

Infrared absorption spectra of unvulcanized natural and synthetic elastomers undergo pronounced changes as the result of thermal or photochemical oxidation. New absorption bands, which appear as the result of oxidation, indicate the presence of hydroxyl and carbonyl groups in the oxidized polymer. From the decrease in intensity of bands associated with the double bonds, the gradual saturation of

double bonds can be observed as oxidation occurs. The spectrum of both natural and synthetic polyisoprene undergo approximately the same changes as GR-S. This suggests that the chemical changes which occur during aging are essentially the same in both polymer systems even though butadiene and isoprene polymers differ with respect to the effect of oxidation on physical properties.

Little is known concerning the oxidation products of vulcanized elastomer. Observed infrared absorption bands indicate that carbonyl and hydroxyl groups are produced.

Antioxidants are consumed during accelerated aging, but the final form into which they are transformed as the result of their inhibiting action is unknown.

G-3745

Bateman, L.

THE PHOTO-OXIDATION OF OLEFINS.

Rubber Age (N.Y.) 63:334-336. June 1948.

Two distinct physical changes that evidence the deterioration of vulcanized rubber surfaces during atmospheric exposure are: exposure cracking, characterized by the development of cracks at right angles to the direction of strain; and sun crazing, resinification of the surface with the formation of an irregular pattern of very fine cracks. Exposure cracking is associated with ozone attack and sun crazing with surface oxidation promoted particularly by the shorter wave lengths of sunlight.

The development of cracks resulting from ozone attack is peculiarly sensitive to the degree of tension of a vulcanized specimen. Cracking is negligible when the rubber is under no strain, is greatest at about 20% extension, and decreases sharply with further extension. A small amount of ozone absorbed by unstretched rubber produces a microscopically thin, but extremely efficient, protective film which seals the rubber substrate against further reaction. Under tension this film breaks down and ozone attack, measured by the rate of formation of tiny cracks, increases to a maximum at about 80% extension. Chemical modification of the surface or incorporation of waxes such as Okerin and Heliozone guards against cracking. If sun crazing is not too extensive it gives appreciable protection against ozone cracking; consequently, ozone cracking can be reduced by exposure to factors conducive to sun crazing.

When rubber is dissolved in 'active' solvents or in 'nonactive' solvents containing sensitizers and is then irradiated by visible or ultraviolet light without free access to oxygen, it undergoes a mild type of vulcanization and the solution gels. In the absence of oxygen, free radicals photolytically produced from the active solvents or sensitizers initiate cross-linking. In the presence of oxygen, photooxidation first occurs and causes the usual molecular degradation of the rubber chains; when the oxygen is used up, the oxygenated groups provide photoactive centers for radical formation and the consequent cross-linking. Readmission of oxygen during irradiation invariably causes solubilization of the gel owing to the unavoidable molecular degradation. Antioxidants which react with and destroy free radicals delay gelling. This action is more marked in systems involving oxygenated free radicals.

A study of the photolysis of highly purified rubber in a high vacuum shows that decomposition with concomitant cross-linking occurs even in the absence of oxygen or other potential cross-linking agents. The reaction is so inefficient, however, that any alternative cross-linking mechanism provided by the presence of oxygenated groups always predominates.

G-3921(1-21)

U.S. National Bureau of Standards.

REPORT ON INVESTIGATION OF THE DEGRADATION OF POLYMERS.

REPORTS NO. 1-4,7-9,11,12,14-21, by Gordon M. Kline;

REPORTS NO. 5,6,10,13, by Frank W. Reinhart.

U.S. Quartermaster Corps, Q.M. Project No. C-39-05-03.

September 1947 - January 1948 and May 1948 - August 1949.

Ultraviolet and infrared absorption, mass spectrometry, photomicrography, electron micrography, X-ray diffraction, and other techniques were employed to investigate the behavior of thin films of nylon compositions, GR-S (butadiene-styrene copolymers), and polystyrene under various degradative conditions of exposure.

Nylon

No evidence of significant structural changes in their infrared transmission curves was observed in films of Nylon 4407 and Nylon 4409. The former was formulated from adipic acid, hexamethylene diamine, and caprolactam, and the latter from sebacic acid, hexamethylene diamine, and caprolactam. The films were exposed to the following conditions: 120-hr sunlamp-fog cyclic accelerated weathering test of Method 6021 of Fed. Spec. L-P-406a, 217 hr standard cyclic accelerated weathering; 59 days of outdoor weathering; heating at 100 C in nitrogen or in air, or irradiating with ultraviolet light for 20 hr at 85 C. As judged by ultraviolet transmission curves, Nylon 4409 was affected more by sunlamp-fog exposure than was Nylon 4407.

Viscosity measurements showed that samples degraded by ultraviolet radiation, heat, or outdoor exposure had lower molecular weights than unexposed specimens, indicating that degradation results in chain scission. Corresponding to the lowered molecular weights, the melting points of four Nylon films 4406 - 4410 were lowered by a 168-hr exposure to an S-1 sunlamp but were not appreciably changed by 59 days of exposure on a roof. The splitting and fragmentation of untreated and degraded nylon films in distilled methanol seems also to be associated with the degree of degradation.

Mass spectrometric analysis of pyrolyzed Nylon 4407 and 4409 showed that carbon dioxide was the main degradation product irrespective of the method of oxidation. Evidence was also obtained for a variety of saturated and unsaturated hydrocarbons. About 5% of the degradation products could be analyzed by this method, 95% by solubility.

Photomicrographs of the four types of nylon taken at 600-fold magnification in polarized light revealed differences between unexposed and degraded nylon films but no definite changes in crystallinity.

Electron micrographs, both unshadowed and chromium-shadowed, showed a definite grain structure in both degraded and undegraded specimens of 4407 and 4409. Nylon 4407 which was deteriorated by ultraviolet rays seemed to be composed of crystallites. The heat degraded films showed no extensive changes.

In X-ray diffraction patterns Nylon 4407 exhibited more crystallinity than Nylon 4409; degraded patterns showed no change in crystallinity.

Polystyrene and GR-S

Because of the sensitivity of GR-S latex Type II to oxidation, one method was developed for making thin, unsupported films in an inert atmosphere, and another method for storing the polymer under carbon dioxide. Wavelengths below 3200 Å apparently are detrimental to this polymer.

Holes and edge shrinkage which usually develop when unirradiated GR-S films are heated in air at 100 C for about 11 hr may be prevented by irradiating for 1 hr with an RS sunlamp. Previous exposure to black light (BH-4 lamp) or to visible light is not a preventive.

Reactions of free radicals in GR-S film were determined by treating the hydrocarbons with activated hydrogen produced by photosensitizing mercury with a cold-quartz mercury lamp (radiant energy of 2637 Å) at 100 C. The degradation products from irradiation in the presence of mercury were insignificant in amount but similar in kind to those obtained by RS-sunlamp irradiation at 100 C. At 200 C larger yields of volatile hydrocarbons were obtained than in vacuo at the same temperature. The infrared patterns of the mercury-photosensitized films showed no extensive changes; no hydroxyl or carbonyl bands were observed. Viscometric studies to detect changes in the molecular weight due to these free-radical reactions could not be made because all GR-S films became insoluble in toluene as a result of their mercury-photosensitization.

Films of GR-S aged in the presence of oxygen either in an oven or by ultraviolet irradiation showed identical infrared oxidation patterns, regardless of the experimental conditions to which they had been previously subjected while undergoing photosensitization at 200 C.

GR-S films exposed either to a temperature of 100 C in an air oven or to S-1 sunlamp irradiation in air at 60 C hardened after 5 hr, and infrared patterns indicated that extensive degradation had occurred. Pure polystyrene exposed to the same conditions was not extensively degraded; this suggests that the polystyrene content may play a minor part in the degradation of GR-S hydrocarbon.

Both polystyrene and GR-S films show a yellowish-green fluorescence under ultraviolet irradiation after oxidative degradation. No changes in infrared transmission were observed in thin films of stretched and unstretched GR-S exposed to ten times the normal atmospheric concentration of ozone, or in polystyrene heated in an air oven at 100, 125, and 150 C for various periods.

Mass spectrometric analyses of the decomposition products of twelve GR-S films heated in vacuo at 100, 140, and 180 C with and without ultraviolet irradiation revealed that excessive amounts of water is present either as a result of water absorption by the film or of hydroperoxide decomposition. Other components identified included carbon dioxide, benzene, propane, acetone, butenes, pentadienes, and diethyl ether.

Polystyrene films remained soluble in toluene after 216 hr air-oven aging at 120 C, but became insoluble after 202 hr exposure to S-1 radiation at about 60 C.

Heat aging of polystyrene films cast from toluene solution produced octane and octene. Addition irradiation with ultraviolet light also

gave benzene and hydrogen. Excessive toluene solvent was always found in the mass spectrogram.

A series of twelve polystyrene films cast from 2-butanone became brittle as the solvent was evaporated.

Films of polystyrene, polymerized at 120 C and purified, evolved appreciable amounts of gaseous products after 5-hr exposure at 140 C and to RS lamp radiation, both in vacuo and in the presence of oxygen. Benzene, hydrogen, water, styrene, and oxygenated products were identified after both 5- and 10-hr irradiation.

Polystyrene films exposed to S-1 sunlamp radiation at 60 - 65 C for 70 hr in air showed an infrared absorption band characteristic of the carbonyl group and, upon prolonged exposure, of the hydroxyl group. The heat-exposed film did not show these groups after 200-hr exposure in air.

Polystyrene films from a commercial polymer evolved amines and formates after 5-, 25-, and 48-hr exposure at 140 C in vacuo with and without RS-sunlamp irradiation, but did not show extensive changes in infrared transmission.

Further investigations are in progress.

G-4261

Throdahl, M.C.

PHYSICAL ASPECTS OF THE AGING OF RUBBERS.

Am. Soc. Testing Materials, Spec. Tech. Publ. 89:35-47. 1949.

Some of the physical aspects of the oxidative processes occurring during the aging of rubber and rubber-like materials are reviewed and interpreted.

The general trends of theory and experimental evidence during the past 10 yr suggest that aging or degradation of rubber is a process similar to polymerization. The reactions involved proceed by chain mechanisms, and the changes in physical properties are the sum of several simultaneous processes, partly opposite in character. These are (1) cross-linking, cyclization, and continued polymerization, all of which harden and stiffen the rubber, and (2) chain scission which causes tackiness and loss of tensile strength.

Different rubbers show relatively different degrees of susceptibility to these mechanisms. The relative rates of one or both groups of reactions may be isolated and measured by various methods, including viscosity, sol-gel relationships, stress-relaxation, creep, and permanent set. Infrared absorption methods seem to show qualitatively that the general oxidation mechanism is similar for hydrocarbon rubbers. Heat aging and ultraviolet activation apparently involve different mechanisms.

A bibliography of 36 references is included.

PDC Comment: More specific discussions of oxidative changes in polymers can be found in two other reports recently abstracted by the Center.

- (1) Cole, John O., CHEMICAL CHANGES IN ELASTOMERS AND ANTIOXIDANTS DURING AGING. Presented at the ASTM Meeting March 2, 1949. PDA 7: Plas 74, G-3729
- (2) Tobolsky, Arthur V., OXIDATIVE DEGRADATION OF POLYMERIC MATERIALS. India Rubber World 118:363-364,371. June 1948. PDA 7: Plas 69, G-3763

G-4331

Ball, J.M. and R.L. Randall.

THE EFFECT OF WHOLE TIRE RECLAIMED RUBBER ON THE ACCELERATED AGING OF NATURAL RUBBER AND GR-S.

Rubber Age (N.Y.) 64:718-722. March 1949.

Mixing substantial amounts of reclaimed rubber with either natural rubber or GR-S tends to improve the resistance of rubber stocks to accelerated aging. A high proportion of reclaim is usually better for age resistance than a low proportion. Reclaimed rubber also gives better processing properties and lower volume costs.

Modern whole tire reclaims containing GR-S hydrocarbon tend to be better than their prewar counterparts. Four commercial whole tire reclaims were tested:

<u>RHC</u>	<u>Process</u>
Natural	Alkali
Natural	Neutral
Natural + GR-S	Neutral
GR-S	Neutral

The first two are prewar reclaims, no longer available except in relatively small quantities. The third is the predominating type today.

Each of the four reclaims was mixed in 40:80 and 100:50 ratios with smoked sheet in one test series and in the same ratios with GR-S in another. Phenyl-2-naphthylamine was used in all compounds in the amount of 1% of the rubber hydrocarbons. Adjustments were made for the antioxidant already present in the GR-S.

Five cures, ranging from 10 to 90 min, were made in the press at 287 F and samples of each cure were aged 46 and 96 hr in both an air oven at 100 C and an oxygen bomb at 70 C and 300 psi.

Tensile Strength. Resistance to air-oven aging is greatly improved by reclaimed rubber. The high reclaim compounds are best and the GR-S series ages better than the smoked sheet series. GR-S is equal or superior to prewar natural rubber reclaims.

In the oxygen bomb age resistance is not greatly affected except in the high reclaim smoked sheet series where improvement results. These compounds age better than the corresponding low reclaim compounds and again the GR-S series ages better than the smoked sheet series.

Elongation. In the very severe air oven test, aging on the whole is improved by the reclaim. Reclaims containing GR-S hydrocarbon are equal or superior to those of prewar, except in the low reclaim GR-S series. The GR-S compounds are somewhat better than those containing natural rubber.

Reclaim has a measurable but not pronounced effect on oxygen-bomb aging. With GR-S, the effect is positive, whereas with smoked sheet it is slightly negative. Again the GR-S stocks perform better than the natural rubber stocks.

Hardness. In the air oven the reclaim compounds harden appreciably less than the controls. The modern reclaim gives excellent results. The GR-S compounds harden more than those containing smoked sheet.

In the bomb, the beneficial effect of reclaim is strikingly evident, especially with GR-S; the GR-S stock hardens less than the natural rubber.

G-4424

Cole, John O.
CHEMICAL CHANGES IN ELASTOMERS AND ANTIOXIDANTS DURING AGING.
Am. Soc. Testing Materials, Spec. Tech. Publ. 89:29-34. 1949.

G-4425

Schoch, M.G., jr. and A.E. Juve.
THE EFFECT OF TEMPERATURE ON THE AIR AGING OF RUBBER VULCANIZATES.
Am. Soc. Testing Materials, Spec. Tech. Publ. 89:59-72. 1949.

The effect of temperature on the rate of deterioration in air of typical vulcanizates of natural rubber, GR-S, GR-I, nitril rubber, and neoprene is reported. Between 70 and 125 C the rate of deterioration is dependent on temperature; the temperature coefficient of aging varies between 1.80 and 3.05 per 10 C depending on the composition of the material and the property being measured. This coefficient is nearly always higher when based on tensile strength than when based on elongation or modulus.

The nature of the deterioration of all materials tested is the same between 70 and 125 C with the exception of those vulcanizates which develop a nonhomogeneous cross-section during aging. Above 125 C all the materials appear to undergo a different kind of deterioration. The arrangement of products in order of resistance to aging will probably change with temperature.

The test-tube method of aging is approximately equal in severity to the oven method but its results are not appreciably more reproducible between laboratories.

The data from all cooperating laboratories are presented in tables showing average values of tensile strength, modulus, and elongation for the various aging periods and temperatures chosen. For each temperature, curves of aging-time versus properties were plotted. From the curves were taken the times required at each temperature for the several rubbers to reach an equal state of deterioration. These values were plotted on a logarithmic scale against temperature and the temperature coefficients calculated.

G-4426

Blake, John T.
THE EFFECTS OF LIGHT AND OZONE ON RUBBER.
Am. Soc. Testing Materials, Spec. Tech. Publ. 89:48-56. 1949.

G-4662

Pollack, Louis R., Robert E. McElwain, and Paul T. Wagner.
OXYGEN ABSORPTION OF VULCANIZATES, A MEANS OF EVALUATING AGING RESISTANCE.
Ind. Eng. Chem. 41:2280-2286. October 1949.

The rates at which oxygen was absorbed by two natural and six synthetic rubber stocks were measured by routine volumetric methods. In addition, the course of aging in the oxygen bomb and air oven was followed by periodically measuring the tensile strength and ultimate elongation of each stock. Correlation between oxygen absorption rates and deterioration of physical properties of the stocks is sufficiently close to warrant the substitution of rapid oxygen absorption measurements for longer standard procedures in evaluating aging characteristics.

- G-5243 Braendle, H.A., H.C. Steffen, and J.G. Devender.
ON THE INADEQUACY OF LABORATORY EVALUATION OF NATURAL AND SYNTHETIC RUBBERS.
Rubber Age (N.Y.) 66:177-181. November 1949.
- G-5360 Werkenthin, Theodore A.
ADDITIONAL DEVELOPMENTS IN THE FIELD OF TESTING PROCEDURES FOR THE EVALUATION OF NATURAL AND SYNTHETIC RUBBERS AND PLASTIC ELASTOMERS SPONSORED BY BUREAU OF SHIPS, NAVY DEPARTMENT.
Rubber Age (N.Y.) 66:45-51; 183-188; 305-310. October - December 1949.
- G-5433(3) Roberts, Palmer W.
EFFECTS ON MATERIALS IN ARCTIC COLD. 3. PLASTICS, RUBBER, GLASS, FABRICS, AND LEATHER.
Military Engr. 42:366-369. September/October 1950.
- Plastics
Satisfactory performance of plastic equipment in the arctic is dependent on its design, fabrication, and care and use in the field as well as on the type of plastic employed. As a guide to the selection of the proper base material, a list is given of the important plastics by resin group, resin subgroup, trade name, available form, and commercial uses. Special properties of these resins are noted with particular emphasis on changes occurring as a result of extreme cold.
- Rubber
No commercially available rubber is truly elastic below -40 F. With care, however, some of the newly developed natural rubber products can be used down to this point. Special rubber-like material containing natural and butyl rubber can be used as low as -70 F.
- Ceramics
Ceramics, window glass, laminated safety glass, and structural glass show no visible reaction to cold, and in addition the last three have been designed to withstand thermal shocks of 150 F.
- Fabrics
Untreated and water repellent fabrics give satisfactory service at -40 F. Canvas and heavy materials lose their pliability at low temperatures.
- Leather
Leather stiffens, cracks, and tears easily at low temperatures. Before exposure to extreme cold it should be tanned carefully and treated with shoe oil or lard. Leather and fur clothing for midwinter use away from main encampments should be made of Eskimo-prepared skins in preference to those commercially tanned, because the Eskimo-prepared skins are lighter in weight, warmer, and stiffen less readily.
- G-5675 Moakes, R.C.W. and A.L. Soden.
EFFECT OF PROLONGED STORAGE OF UNVULCANISED STOCK ON THE PROPERTIES OF THE VULCANISATE.
J. Rubber Research 17:30-32. 1948.

G-5683

Scott, J.R.

AGEING OF GR-S VULCANISATES. 3. SOME EFFECTS OF OXYGEN AND TEMPERATURE ON AGEING.

J. Rubber Research 18:117-123. November 1949.

At high temperatures (135-153 C) the decrease in tension strength and elongation and the increase in stiffening of GR-S vulcanizates were accelerated by the presence of oxygen. At 70 C the same effect was produced by raising the oxygen pressure from 0.2 to 20 atm. When the rubber was undervulcanized, however, increasing the oxygen pressure often resulted in less stiffening, and also caused the aged rubber to retain more set after stretching. At 80 C, raising the oxygen pressure from 0.2 to 20 atm did not promote stiffening even in well vulcanized rubber, and sometimes even reduced it.

In air-aging tests at 100 C for 60 days the tension strength of GR-S vulcanizates reached a constant value or even increased eventually; however, the vulcanizates became progressively stiffer and less extensible. Under hot service conditions, therefore, GR-S is more likely to fail through inability to stretch than through loss of strength.

From these results, which agree with those of previous investigators, the following conclusions were drawn:

- (1) Oxidation, in addition to promoting loss of strength, is one of the causes of stiffening of GR-S during aging, presumably because of oxygen bridging between the molecules.
- (2) Oxidation can also cause softening, probably by chain-scission, and thus changes the shape of the stress-strain curve and increases set after deformation.
- (3) At temperatures above 80 C, increase of oxygen pressure, as in the bomb test, favors the softening rather than the stiffening reaction, especially in undervulcanized rubber; below 70 C this effect is not observed. This behavior casts doubt on the value of a high-temperature oxygen bomb test for simulating the natural aging of GR-S.

G-5684

Elliott, R. and R.G. Newton.

FACTORS CONTROLLING THE RESISTANCE TO EXPOSURE-CRACKING OF NATURAL AND SYNTHETIC RUBBERS, WITH SPECIAL REFERENCE TO GR-S.

J. Rubber Research 17(2):17-29. February 1948.

G-5748(1-2)

Newton, R.G. and W.C. Wake.

LIGHT STIFFENING OF RUBBER.

J. Rubber Research 19(2):9-16; 19(3):17-27. February - March 1950.

Light-stiffening is the noticeable increase in bending modulus of thin sheets of rubber or single-texture proofings on exposure to light and air. It is a light-catalyzed oxidation proceeding by a free-radical chain mechanism that can be accelerated by heat. Light-stiffening can be prevented by antioxidants and/or deactivators, which interfere with the propagation of the reaction chain. The service life of rubber sheets or proofings can be increased by protecting them from ultraviolet light. If exposed only to light of long wave length, viz., green, yellow, or

red, light-stiffening would be almost completely prevented. The type of polymer, thickness and color of the proofing, and temperature are of significance in light stiffening; mode of vulcanization and wax content have little influence.

A simple test is described for measuring the increase in bending modulus of light-weight proofings and of rubber films up to 80 μ thick. It is rapid and more sensitive than previous tests in following changes resulting from outdoor exposures.

The effect of light-stiffening decreases from surface to interior. Light-stiffening is followed by the formation of a resinous surface film, which involves contraction of the surface and hence surface crazing when the material is sufficiently rigid to resist the resulting tendency to curl.

Stiffness of standard GR-S rubber samples stored in the dark increased 100% in about 3 yr. On 20 days exposure to sunlight, stiffness increased at least 850%; on long exposure, 2000-6000%.

The relative amounts of stiffening in various months of the year were different; there was a 20-100 fold difference between winter and summer. This variation is due to changes in total amount of light received by the samples and the effect of heat in summer.

The stiffening of GR-S proofing was not appreciably affected by a change in wax content, but decreased with increasing thickness and varied with color: black proofing stiffening least and yellow, most. For neoprene, changes in wax content and thickness were without effect, but color produced differences, with the black proofing stiffening least, although the differences were not as marked as with GR-S. Butyl compounds softened on exposure to light irrespective of thickness, color, or wax content.

Attempts to produce stiffening by using seven artificial sources of light were unsuccessful. Although with one lamp an initial rate of stiffening of nearly 600% per 24-hr day was obtained, as compared with the average 70% per 10-hr day caused by summer sunlight, the total amount of stiffening produced by a 50-hr exposure 10 in. from the lamp was only 680%. It is unlikely that a satisfactory artificial source for light-stiffening will be found.

In the modulus test, one end of a strip of proofed fabric of given dimensions is clamped in a metal support in a standard manner and the other end acts as a cantilever sagging under its own weight. Stiffness is assessed before and after exposure to sunlight by a determination of the effective bending modulus from the deflection in centimeters of the end of the cantilever below the horizontal. As the sample stiffens, known weights of bent pieces of wire are hooked into the end of the sample in order to produce measurable deflections. The modulus depends on the weight and on the cube of the thickness of the proofed fabric.

G-6032

Nellen, A.H. and others.

THE EFFECT OF ATMOSPHERIC OZONE ON TIRES DURING STORAGE.
Rubber Age (N.Y.) 66:659-662. March 1950.

A nation-wide survey of the degree of ozone attack on tires under various storage and climatic conditions showed the following:

- (1) Unprotected tires stored or displayed outdoors under any tension tend to crack, and the degree of cracking varies in different localities.

- (2) Tires stored in unventilated masonry buildings deteriorate less than those stored in metal warehouses.
- (3) Wrapping tires in paper is the most satisfactory means of protection.

Samples in the exposure test consisted of 6.0- by 0.50- by 0.25-in. pieces of X-478 cold rubber with 50 PHR of HAF black reinforcement. The samples were bisected by a groove, and mounted on a board at angles of 15°, 30°, and 60°, to simulate strain in the base of a tire groove. Eighty-seven test boards of samples were exposed indoors and outdoors at fifty-five locations throughout the United States, for an average of 45 days. They were then compared with a standard set of samples exposed in a laboratory ozonizer having an ozone concentration of 4.4 ± 0.2 ppm. The set of standards was exposed in 30 min increments over a range of 8 hr. To each sample exposed indoors or outdoors a numerical rating was assigned, equal to the total exposure in minutes of the standard with which it compared. The minimum rating for samples exposed outdoors was 300. Samples exposed in warehouses varied from less than 30 to 420.

The Southern California and Denver atmospheres represent the highest concentrations of ozone in the country; the Boston area, the Gulf Coast, and Texas atmospheres are also fairly high in ozone. The North Pacific Coast and the Midwest show considerably less ozone, and the lowest average is in the Middle Atlantic States.

A tire section wrapped with kraft paper of 90-lb basis weight was completely protected when ozonized 12 hr; an unprotected section showed severe checking. Paper-wrapping is more effective than incorporating a protective compound in the rubber, or painting it. These last measures give satisfactory protection in storage but in subsequent service, fractures in the coating or bloom localize the ozone attack, resulting in deep cracking.

Since tire treads and sidewalls of large trucks are stiff and rigid, they are not subject to strains in storage and consequently do not require wrapping.

G-6080

Reynolds, W.B.
COLD RUBBER.

J. Chem. Education 27:494-499. September 1950.

G-6128

Metz, Donald J. and Robert B. Mesrobian.

THE EFFECT OF VULCANIZING AGENTS ON THE HEAT DETERIORATION OF NATURAL RUBBER.

Brooklyn. Polytechnic Institute. Technical Report No. II on
U.S. Office of Naval Research Contract N6onr-26309. May 1949.

The effects of amounts and/or types of vulcanizing agents on the absorption of oxygen and on stress decay of ten differently compounded natural-rubber gum vulcanizates were studied. The molecular weight between cross links of each sample was determined and this value was used to calculate the rate of total chain scission from stress relaxation and also the ratio of oxygen absorbed to chain scission.

The accelerators diphenylguanidine (D.P.G.), tetramethylthiuram disulfide (Tuds), and monosulfide (Monads) markedly decreased rates of

oxygen absorption and stress decay of the vulcanizates when compared with mercaptobenzothiazole (Captax) and benzothiazyl disulfide (Altax).

In the absence of accelerator, zinc oxide had little effect on the heat deterioration of the vulcanizates, but in the presence of accelerator greatly retarded heat deterioration.

Changes in sulfur concentration had only a slight effect on the extent of heat deterioration. At intermediate sulfur concentrations the rates of oxygen absorption and stress relaxation were greatest.

The ratio of mols of oxygen absorbed to mols of chain cuts was close to unity for all the vulcanizates studied, despite their large respective differences in oxidation and stress relaxation rates.

At high temperatures (134 C) the rates of oxygen absorption of all samples were nearly identical. This indicates that the largest separation in values occurs at low temperatures and further corroborates earlier studies that proposed the existence of maximum steady rates of oxidation.

The use of artificial aging tests for interpreting the effect of chemical agents on the heat deterioration of rubber may lead to false inferences unless the rubber samples being compared are initially in the same physical state. For a vulcanized rubber this is the initial molecular weight between the cross links.

Oxygen absorption measurements of the various vulcanizates were carried out at constant pressure in a static system. Continuous stress relaxation at 50% elongation was determined with a beam-balance stress relaxometer. Measurements were made at 75, 100, and 134 C.

G-6142

Crabtree, James and F.S. Malm.

DETERIORATION OF RUBBER FROM USE AND WITH AGE.

To be published by Reinhold Publishing Corporation as Chapter 6 in "Rubber in Engineering," edited by A.T. McPherson.

Breakdown of the rubber structure may be brought about by mechanical fatigue or by chemical change. Chemical changes can be caused by the effects of elevated temperature, atmospheric oxygen, ozone, and bacterial attack. Heat is the factor of greatest overall importance. All factors are influenced to some degree by relative humidity and liquid water. The complicated interconnections of all these variables make quantitative estimates of service performance difficult.

Elevated temperature

Heat shortens the life of rubber products in three ways: (1) it doubles the rate of oxidation for every 8.7-C rise in temperature; (2) it brings about continued vulcanization which leads to overcuring with consequent stiffening and increased susceptibility to oxidation, particularly in rubbers containing uncombined sulfur; and (3) it causes pyrolysis which proceeds slowly at temperatures only slightly above those used for vulcanization, but rapidly at 350-400 C.

Silicones, Teflon, and other synthetic polymers were developed for continuous use at temperatures which rapidly destroy a conventional rubber compound.

Atmospheric oxygen

The physical effects of oxidation cause a decrease in tensile strength, resilience, elongation at break, and increase in hardness or softness, creep, and permanent set.

Oxidation proceeds autocatalytically via chain reactions in which free radicals combine with oxygen to form peroxide compounds. These compounds react with the parent hydrocarbons to form more stable products and liberate other free radicals to repeat the cycle. Oxygen in an amount equal to 1% of the weight of the rubber can produce almost complete loss of elastic properties, because when one molecule of oxygen breaks a double bond, the molecular weight of the rubber is cut in half (about 300,000).

The rate of oxidation is slow at ordinary temperature in air, and in water, oil, or other low-oxygen or oxygen-free media. It is practically unaffected by the degree of rubber stretch, but greatly accelerated by rise in temperature and by absorption of sunlight; the latter catalyzes the production of free radical chains through photolysis of the peroxidic substances in a manner similar to but faster than heat. The rate of oxidation also increases with the rate of oxygen diffusion, with degree of unsaturation and vulcanization of the rubber molecule, carbon black content, the presence of certain multivalent metals, notably copper and manganese, and, for a given cure, with combined sulfur.

Resistance to oxygen aging can be enhanced by (1) protecting the unsaturated bonds of synthetic rubbers through the introduction of electrophilic side groups, such as phenyl (butadiene-styrene), cyanide (Perbunan, Hycar), and chlorine (neoprene); (2) by using curing accelerators which permit vulcanization with low sulfur content; and (3) by adding about 1% of antioxidants, which react preferentially with peroxidic bodies and oxygenated free radicals, thus curbing the production of free radicals. Unfortunately, the most effective antioxidants give strongly colored oxidation products and do not protect against light sensitization. In rubbers that use carbon black as reinforcement, the black acts as an efficient opacifier making the light reaction unimportant. Light-colored compounds containing zinc and titanium oxides, although initially reflecting much of the actinic radiation, are subject to photo-degradation causing chalking, cracking, and peeling of the rubber. A certain degree of protection is given by ultraviolet absorbing salicylates and similar sun-screening additives.

The only reliable criterion of rubber performance is the actual service trial. Accelerated tests can be used as a guide only if some standard compound of known service performance is included in the study. Accelerated tests usually involve high-temperature oxidation, carried out in a circulatory air oven, in an oxygen bomb, or in an oil bath; degradation may be assessed by measuring either changes in mechanical properties or actual amounts of oxygen consumed. Correlations of high-temperature tests with service performance are better for articles maintained at more or less uniform high temperatures for prolonged periods, than for items exposed under variable temperature and weathering conditions, since it is practically impossible to duplicate weathering factors, especially the effects of light.

Atmospheric ozone

Ozone reacts with the double bonds of rubber molecules much more energetically than does molecular oxygen. Rubber in solution is completely decomposed, but solid vulcanized rubber, in the relaxed state, can be exposed to relatively high ozone concentrations for long periods without effect, probably because its surface becomes passivated by a film of ozonide. In rubber stretched as little as 2-3%, however,

cracks, vertical to the direction of stress, appear when the atmosphere contains as little as 0.01 ppm of ozone. The rate of cracking increases with increasing ozone concentration and as little as 0.01% will completely rupture stretched vulcanized rubber in a few minutes. Unlike oxygen aging, the attack is not uniformly distributed but is strictly localized, the rubber between the cracks retaining all its initial properties. Molded rubber articles exposed to ozone lose gloss, especially in the presence of high relative humidity.

Increasing the elongation at a given temperature, as well as increasing the temperature at a given stress, increase the number of cracks produced by a certain ozone concentration. Low temperatures delay, but do not eliminate cracking, which occurs almost to the freezing point of the rubber.

Ozone concentration is lower in equatorial regions than in higher latitudes and, in the latter, about 30% less in fall than in the spring. Indoor ozone concentrations are usually low provided there is no appreciable ventilation. Rubber goods stored in freely ventilated locations should always be covered.

Natural rubber, Perbunan, and GR-S cold rubber are most susceptible to ozone cracking; GR-S and Hycar have a little more resistance; Neoprene is fairly resistant, and Butyl rubber is almost completely inert. Gum compounds are the most resistant to ozone. Any diluent, whether inert or reinforcing, aggravates ozone damage; blending with a less resistant rubber also increases ozone susceptibility.

Rubbers under static stress can be fairly well protected by incorporating about 5% microcrystalline waxes of the straight chain paraffin type; these exude slowly to the surface where they form a continuous barrier film. If not enough wax is added, or if it does not form the right type of film, or if it is incompatible with some rubber constituent, or if the rubber is under dynamic stress, the addition of wax can be useless or even damaging. Effective ozone inhibitors such as substituted dimethylpyrroles, also act by blooming to the surface and, upon oxidation, form a tough horny or gummy barrier film. Unlike wax, they are not affected by temperature and are effective in dynamic flexing. Their useful life is limited, however, because they are rapidly oxidized and thus consumed.

There is no standard accelerated test for measuring ozone susceptibility. Of the two current practices, visual estimation of the amount of damage is more subject to personal error than measuring the time elapsed before cracks are observable under a fixed magnification.

Abrasion

The rate of wear of a given rubber compound depends on the load, speed, slip, angle, and the continuous or intermittent nature of abrasion, as well as on temperature, humidity, and the nature of the abrading surface. Increased abrasion resistance may be obtained by using reinforcing carbon blacks, stearic acid, waxes, softeners, and other additives. Inert loadings, such as clay and whiting, and breakdown by aging all tend to reduce wear resistance.

Microorganisms

Fungi are not a significant cause of rubber degradation. Two types of bacteria, however, one utilizing hydrocarbons as nutrient source, the other oxidizing free sulfur to sulfuric acid, can cause a certain amount of breakdown, along with a decrease in electrical resistivity of rubber insulation, especially under warm moist conditions. Natural rubber is most susceptible, GR-S and Butyl rubber less so, and Neoprene is apparently quite resistant to bacterial attack.

Deterioration of ebonite

Hard rubber, which contains about 30% sulfur nearly all in combination presumably at the double bonds, is much less reactive and has a lower gas permeability than soft rubber. Hard rubber is practically unattacked in the dark at ordinary temperatures; however, increase in temperature and/or exposure to sunlight lead to rapid deterioration of the surface with formation of sulfuric acid and brownish oxidation products, with consequent losses in impact resistance and electrical resistivity. Deterioration caused by light is reduced by incorporating calcium or barium carbonate in amounts at least 50% of the chemical equivalent of sulfur present. GR-S and Perbunan hard rubbers behave similar to natural hard rubber. Neoprene does not form a hard rubber compound.

G-6397

Mark, Herman F. and Robert B. Mesrobian.
THE EFFECT OF OXYGEN ON THE PHYSICAL AND CHEMICAL PROPERTIES OF
POLYMERS.
Brooklyn. Polytechnic Institute. Institute of Polymer Research.
Interim Report No. V on U.S. Office of Naval Research
Contract N6onr-26309. January 1950.

G-6400

National Research Council. Advisory Board on Quartermaster Research
and Development. Committee on Plastics and Elastomers.
Subcommittee on Rainwear.
MINUTES OF MEETING, 13 DECEMBER 1950, submitted by Frank Y. Speight.
January 1951. 10 p.

G-6564

Dawson, T.R. and L.A. Doyle.
PROTECTION OF VULCANISED RUBBER AGAINST WHITE ANTS.
J. Rubber Research 19:101-105. September 1950.

G-6608

Clark, Richard A. and John B. Dennis.
COMPOUNDING ACRYLONITRILE-TYPE RUBBER FOR LOW TEMPERATURE FLEXIBILITY.
Ind. Eng. Chem. 43:771-778. March 1951.

A study was made of the effect of type of vulcanizing system, type and amount of carbon black, and ratio of carbon black and plasticizer on the low-temperature flexibility of Paracril 18-80 stocks. The effect of immersion of the stock in AN-VV-0-366B hydraulic oil was also studied. For applications involving exposure to both low temperature and oil, minimum levels of plasticizer and carbon black are recommended to effect a compromise between hardness, swell, and low-temperature flexibility.

The choice of vulcanizing system had only a small effect on low-temperature flexibility. The greater the carbon black loading, the greater the hardness and the poorer the low-temperature flexibility. In heavily loaded stocks of equal hardness, carbon blacks of fine particle size produced increased stiffness at low temperatures; MT, SKF, and MAF blacks were best, HAF black was intermediate, and EPC black was poorest in low-temperature flexibility. The addition of

both carbon black and plasticizer tended to improve low-temperature flexibility, but the improvement decreased with increasing hardness, and became negligible at a durometer hardness of about 85. In stocks of equal hardness, the presence of a plasticizer contributed nothing to flexibility until temperatures below -20 or -30 C were reached. Differences in low-temperature flexibility between stocks of the same hardness but varying widely in carbon black and plasticizer loading were substantially reduced by aging in a petroleum-base hydraulic fluid.

G-6664

PROPERTIES OF CHEMICAL ENGINEERING MATERIALS OF CONSTRUCTION.
Ind. Eng. Chem. 42:2026-2076. October 1950.

Mechanical, electrical, thermal, optical, and physical properties, resistance to chemicals, and manufacturing data are compiled in tabular form for aluminum alloys, iron, mild and low-alloy steels, nickel and high-nickel alloys, tin and tin alloys, titanium, and tantalum, as well as for cements, elastomers, plastics, hard rubber, synthetic fibers. Emphasis is placed on data indicative of resistance to both natural and artificial corrosive agents. Resistance to biological agents is also included for some materials. A well defined code system is used to indicate methods of fabrication, form of the material, applications, and metallurgical treatments.

This compilation supplements and/or revises a previous tabulation issued in October 1948. Extensive bibliographies are included.

G-6813

Stafford, R.L.
SOME OBSERVATIONS ON THE OXIDATION OF RUBBER IN LIGHT.
Rubber Chem. and Technol. 23:404-413. 1950.

G-6852

Whorlow, R.W.
STUDY OF THE MECHANISM OF SURFACE DETERIORATION OF EBONITE AND OF
MEANS OF PREVENTING DETERIORATION.
J. Rubber Research 19:115-123. November 1950.

The deterioration of the surface resistivity of ebonite caused by a particular quantity of light increases with decreasing intensity of illumination. From the results of exposure to different types of radiation it is concluded that the surface temperature of ebonite during exposure is the most important variable causing the difference. The observed effects are explained by assuming that sulfurous acid is produced as an intermediate product in the deterioration, and that this may either decompose to sulfur dioxide and water, or oxidize to sulfuric acid. Decomposition into sulfur dioxide and water, accompanied by volatilization is favored by higher temperatures during radiation, whereas oxidation to sulfuric acid is favored by lower temperatures.

Only light having a wave length less than 5700 A causes any detectable deterioration. Deterioration is most rapid at 75-90% RH. It is postulated that moisture and oxygen must be adsorbed simultaneously on ebonite to cause deterioration in the presence of actinic light.

Possible methods of preventing or reducing deterioration are discussed, and it is concluded that the only method likely to be effective is the application of an opaque surface coating, possibly incorporating a suitable basic material to neutralize any acid formed. This method can be applied only where it is permissible to alter the appearance of the surface and to reduce the initial surface resistivity to a relatively low value. It was shown experimentally that a bakelite layer 1 mm thick which excluded light and restricted access to air was satisfactory except that it gave an effective surface resistivity of only $10^{11} \Omega$. The incorporation of a basic compound to neutralize the acid was not effective except possibly when the formation of acid was slow or when the compound was used in combination with a surface coating. When coating the surface is impractical, the use of an antioxidant might be considered; however, only limited improvement has been achieved by this means. The best antioxidant tested, sym-di-2-naphthyl-p-phenylenediamine, increased the time required to reach $10^{11} \Omega$ by about 2.5 times.

The ebonite in the tests was prepared by vulcanizing 68 parts unaccelerated natural rubber and 32 parts sulfur for 7 hr at 155 C. Strips of the cleaned ebonite were mounted with colloidal graphite electrodes in medium hard glass tubes containing a small amount of moist sodium chloride to maintain 75% RH. The light source was a tungsten filament lamp or a quartz mercury-vapor lamp. Surface resistivity was measured with a Lindemann electrometer after 5-min electrification at 500 v.

G-6945

Svetlik, J.F. and L.R. Sperberg.

THE T-R (TEMPERATURE-RETRACTION) TEST FOR CHARACTERIZING THE LOW-TEMPERATURE BEHAVIOR OF ELASTOMERIC COMPOSITIONS.

India Rubber World 124:182-187. May 1951.

The temperature-retraction (T-R) test affords a complete characterization of the low-temperature properties of an elastomer in a shorter time than does any other test method or combination of methods. The T-R test is simple, versatile, and gives results that are highly reproducible.

The T-R test is an extension of the standard Scott T-50 test and utilizes the same equipment. Temperatures corresponding to retractions of 0, 1, 2, 3, 5, 10, 20, 30, 40, 50, 60, 70, 80, and 90% after different elongations are recorded. Temperature retraction curves are drawn and the temperature at zero retraction is extrapolated.

When the method was applied to butyl rubber, nitrile rubber, GR-S, neoprene, polybutadiene, and natural rubber vulcanizates, using 50% elongation, there was good agreement with results obtained by the torsion modulus technique. The T-R test thus measures the second order transition temperatures of elastomeric compounds.

Although the extrapolated freezing point of an elastomer is not appreciably affected by test elongation from an operational viewpoint, an extension of 50% is preferably employed. The optimum elongation that should be used when determining the tendency of an elastomer to crystallize in cold storage is 50%. To determine if an elastomer crystallizes on stretching, the test must be made at a series of elongations; a minimum of two test elongations such as 50 and 200-300% should be employed.

Materials that crystallize almost immediately at low temperatures are readily recognized by their sluggish retraction characteristics, whether the crystallization is spontaneous or is induced by cold storage or by extension.

G-7189

Blow, Claude Montague and R.G. Newton.
RUBBER TEST METHODS; A REPORT OF THE 1950 ISO MEETING.
Trans. Inst. Rubber Ind. 27:166-174. June 1951.

G-7228

Villain, Henri.
THE ACTION OF COPPER AND ITS DERIVATIVES ON THE AGING OF RUBBER.
Rubber Chem. and Technol. 23:352-361. April/June 1950.

A study was made of the effect of powdered copper, and of various inorganic and organic copper compounds on the aging of two pure gum rubber stocks. Composition of the vulcanizing system, as well as the influence of fatty acids, and of anticopper compounds were also examined.

All of the copper compounds except copper phthalocyanine and copper dimethyldithiocarbamate increased, to a dangerous extent, the rate of autoxidation of the rubber mixture in natural or accelerated aging tests. The copper compound in each case was added in an amount sufficient to give a copper content of 0.02 and 0.06% by weight of the rubber. Each copper reagent had an action different from the other, but all fell in the same order regardless of accelerator or copper content; the greater the tendency to ionize and/or dissolve in rubber, the greater the aging effect. The copper salts of fatty acids and halides had particularly bad effects. In the presence of 0.02% copper, for example, the mixtures accelerated with mercaptobenzothiazole and containing copper powder, oxide, or sulfide lost only 25-28% of their tensile strength after 12 days in a Geer oven at 70 C, as compared with a 36-47% tensile-strength loss for mixtures containing copper chloride, sulfate, acetate, stearate, or resinate. Aging was more rapid with the acid accelerator diphenylguanidine than with the basic accelerator mercaptobenzothiazole. It was impossible to use the basic accelerator in the oxygen bomb tests because destruction was complete in 8 hr or less.

Certain ingredients, notably tetramethylthiuram disulfide, neutralized the deleterious action of copper. Fatty acids increased this action but were not a requisite for the process of degradation by copper. In an oxygen bomb test at 70 C and 20 kg per sq cm, a mixture containing 0.02% of copper as copper acetate and 4% stearic acid lost 90% of its tensile strength in 48 hr, whereas the control containing only the copper lost 50%.

From a practical viewpoint, protection against copper can be accomplished effectively by means of certain anticopper agents such as Agerite White, BLE Powder, and disalicylaldehydethylenediamine. The combined use of 0.5% disalicylaldehydethylenediamine and 0.5% phenyl-2-naphthylamine gave the maximum protection. A vulcanizate containing this mixture and 0.02% copper as stearate, retained 75% of its tensile strength after 12 days in a Geer oven; a control containing only 0.02% copper was destroyed, and one containing 0.02% copper and 0.5% disalicylaldehydethylenediamine retained only 15% of its tensile strength.

G-7319

Russell, E.W.

THE CRYSTALLIZATION OF VULCANIZED NATURAL RUBBER AT LOW TEMPERATURES.
Trans. Faraday Soc. 47:539-552. May 1951.

A series of natural rubber vulcanizates have been crystallized at -36, -26, -17.5, and -2 C and the changes followed dilatometrically. Raw rubber shows a maximum rate of crystallization at about -26 C; vulcanization decreases the rate and alters the shape of the temperature-rate curve. The amount of combined sulfur present in the rubber is the chief factor in determining the rate and extent of crystallization of pure gum vulcanizates. Cross-linking, where the chains between the cross-links are chemically unaffected, also depresses the rate and extent of crystallization.

The use of vulcanizates that crystallize slowly permits melting at much lower rates of heating than was previously possible with raw rubber. Two stages of melting are distinguished, the first occurs under the influence of forces between the crystalline and amorphous regions, and the second occurs in a manner analogous to the melting of low molecular weight crystalline substances.

The rubber compounds selected for this study were simple gum stocks comprising only rubber and vulcanizing agents. They varied only in the proportions of sulfur and/or accelerator used, and in the nature of the accelerator used. Five types of mix comprising seventeen different vulcanizates were studied. Volume changes produced by crystallization were measured in mercury-filled dilatometers as recommended by Bekkedahl and Wood.

G-7337

PROPERTIES AND APPLICATIONS OF FILMOGENS.

Modern Packaging Encyclopedia 1952, p. 285. Report consists of a table.

G-7340

PROPERTIES OF PACKAGING FILMS.

Modern Packaging Encyclopedia 1952, p. 278-279. Report consists of tables.

G-7370

Fisher, Harry L.

ELASTOMERS.

Ind. Eng. Chem. 43:2227-2235. October 1951.

G-7379

Biggs, B.S.

DETERIORATION OF ORGANIC POLYMERS.

Bell System Tech. J. 30:1078-1102. October 1951.

G-7391

Morris, Ross E., Joseph W. Hollister, and Frank L. Shew.

BUTADIENE POLYMERS FOR LOW TEMPERATURE SERVICE.

Ind. Eng. Chem. 43:2496-2500. November 1951.

The cold compression set test at -35 F was used to evaluate the suitability of thirty-four experimental butadiene-styrene copolymers for arctic gasket service. The specimens were prepared by a recipe

designed to permit differentiation of rubbers from the standpoint of hardness and compression set without interference from carbon black structure or rate of cure of the rubber. Six copolymers yielded vulcanizates having stable compression sets lower than that of standard GR-S vulcanizate. Their polymerization temperatures ranged from 86 to 145 F and their contents of combined styrene from 8.7 to 16.0%. The polymerization temperature of standard GR-S is 122 F and its combined styrene content is 23.5%. The six low styrene compounds are considered more suitable for low temperature service than are regular GR-S or GR-S10 stocks.

Some polybutadienes and copolymers of low styrene content underwent a rise in compression set between 5-94 hr conditioning, indicating the occurrence of crystallization. Some, however, had very high compression sets after 5 hr and these were increased only a small amount or not at all after 94 hr. Crystallization in a gasket causes hardening and is incompatible with proper sealing ability. Internal viscosity is responsible for the cold compression set of rubbers that do not crystallize and is a direct function of combined styrene if other characteristics are the same. Excessive internal viscosity, however, can be as harmful as crystallization.

Strip specimens of a GR-S 40 AC vulcanizate containing 43.0% combined styrene and polymerizing at 122 F readily broke when tested at -35 F after being conditioned for 7 days at this temperature. This vulcanizate had slightly more than 100% set after 5-hr conditioning due to its high intrinsic viscosity and thermal shrinkage. In contrast, a vulcanizate of a 100% butadiene rubber polymerizing at 14 F did not break when tested under similar conditions although it also reached 100% compression set at this temperature. Thus crystallization does not make a rubber brittle even if it results in 100% compression set.

Vulcanizates of some low styrene copolymers prepared by a practical recipe containing tris(2-ethylhexyl) phosphate plasticizer were at least equal to GR-S10 (22.9% combined styrene) in tensile properties and some exceeded it in tensile strength. The low styrene copolymers had about the same hardness at 82 F as GR-S10 but they were softer at -35 F. Their cold compression sets were 30-50% lower than those of similar, nonpractical vulcanizates made without the phosphate plasticizer.

PDC Comment: The following reports on this subject have also been abstracted by the Center:

- (1) U.S. Naval Shipyard, Rubber Laboratory, Mare Island. COLD RESISTANCE OF VULCANIZATES PREPARED FROM VARIOUS BUTADIENE AND BUTADIENE-STYRENE ELASTOMERS. Report 69-34, 11 l., October 1949; PDA 8:Plas 132, A-845
- (2) U.S. Arsenal, Rock Island. BUTADIENE POLYMERS FOR LOW TEMPERATURE SERVICE. Report 12, 20 l., March 1949, PDA 8:Plas 16, A-762
- (3) R.D. Juve and J.W. Marsh. LOW TEMPERATURE BEHAVIOR OF BUTADIENE-STYRENE COPOLYMERS. Ind. Eng. Chem. 41:2535-2538 (1949); PDA 8:Plas 75, G-5418

G-7401

Cotton, F.H. and K.O. Lee.
EFFECT OF STORAGE OF MILLET RUBBER ON ITS MOLECULAR WEIGHT.
India Rubber J. 120:919-920. June 1951.

G-7449

Malcolmson, R.W.
NEOPRENE APPLICATIONS IN ENGINEERING DESIGN.
American Society of Mechanical Engineers, New York, N.Y.
Paper No. 51-SA-37. 1951. (Also published in Mech. Eng. 73:
627-632, 643. August 1951.)

G-7493

Shaw, Robert F. and S.R. Adams.
NONDESTRUCTIVE AGING TESTS FOR RUBBER.
Anal. Chem. 23:1649-1652. November 1951.

Several nondestructive methods have been devised for correlating natural aging and service life of rubber. In the most successful, the strain-test method, the test specimens are subjected to definite loads or extensions at repeated intervals during exposure to the deteriorating influence of heat, light, air, and ozone. The degree of deterioration is evidenced by an increase in elongation for specimens that become cracked and by a decrease in elongation for those that become heat-hardened. The test data are obtained on the same specimen at varying time intervals. They are reproducible, and are measured in the usual low-elongation service range (0-150%). The results are expressed as a numerical quantity.

Test strips, 0 by 0.25 by 0.080 in., are hung in an air oven or stretched in a special plastic rack in an ozone cabinet. The stretch rack allows air or ozone circulation around the specimen and can be adjusted to any desired rate of extension. In the examples cited, measurements were made at 200 and 400 psi and at 158 and 212 F.

As evidenced by both artificial and natural aging methods, loss in elongation is probably the greatest factor in failure of rubber items. In oven tests the greatest loss occurred in the first ten days.

The electrical resistivity and the reverse modulus methods for rubber aging are also briefly described.

G-7501

Soden, A.L. and W.C. Wake.
DETERIORATION OF RUBBER UNDER THE INFLUENCE OF LIGHT AND DRY AND
MOIST HEAT.
Trans. Inst. Rubber Ind. 27:223-231. August 1951.

The natural aging of rubber under dry and moist tropical conditions was compared with Geer-oven aging at 70 C under dry conditions, and at 70 C and 100% RH.

Moist heat causes greater deterioration than dry heat, but the damage produced is similar in nature. A simple conversion factor can be used to correlate the results of moist heat and dry Geer-oven aging tests.

Under Geer-oven conditions, moist heat is more severe than under natural tropical conditions; thus, the difference between the results of dry and moist natural aging is much less than that between the results of dry and moist artificial aging.

Even when shielded from the direct rays of the sun, rubber aged under dry conditions in the tropics is influenced more by bright sunlight than it is by heat.

The deterioration of rubber in use or storage in tropical countries depends on the nature of the article. Where the surface layers form a substantial part of the weight of the article, as in rubber proofings, the deterioration is light catalyzed, and the immediate causes of failure are stiffening and subsequent crazing of the surface. In bulk rubber, thermal and moisture effects are more important. Consequently, thin proofings should be protected against light by incorporating a dark pigment filler in the rubber stock. Dark pigments, although they tend to raise the average temperature of irradiated articles, reduce the amount and depth of light penetration. Proofings stored in bright sunlight should be packaged in opaque coverings or in suitably dyed wrappers. For bulky articles and for applications where surface properties are less important, light-colored stock is preferred. Where possible, rubber articles in use or storage in the tropics should be placed in the shade and away from the ground and walls to insure air circulation.

G-7502

Schroeder, Charles H. .

STORAGE STABILITY OF UNVULCANIZED NATURAL, NITRILE, AND GR-S RUBBER COMPOUNDS.

India Rubber World 125:53-54. October 1951.

The storage stability of unvulcanized natural, nitrile, and GR-S rubber stocks is affected by accelerators, retarders, heat history and type of the polymer, individual polymer lots, and by the reaction between polymer and loading pigment. A good indication of the relative storage stability of a rubber stock is given by the plasticity loss of the stock aged at 110 F for varying time periods. This loss may also be used to predict factory processing characteristics after room temperature storage.

Plasticity loss caused by polymer-pigment interaction is affected by type, quantity, and source of supply of the loading pigment, mixing conditions, and storage temperature, and can be overcome by remilling. Unvulcanized rubber stocks that cannot be remilled after aging and before use must be formulated so as to avoid plasticity loss.

In general, most nonblack pigments behave like SRF black in their effect on storage stability, although certain types of whiting and large quantities of zinc oxide (250 phr) behave like HAF black. Carbon blacks with smaller particle size, such as MPC black, impart poor storage stability to rubber compounds.

Rubber batches mixed at as low a temperature as possible become harder during storage than batches mixed hot, even when the hot-mixed material is originally less plastic than the cold-mixed compound. Although the data are not conclusive, it appears that the coefficient of plasticity loss with increasing temperature may vary with the composition of the material involved.

No single retarder appears effective in all formulations. Malic acid is outstanding with nitrile rubbers but does not appear to work so well with GR-S or natural rubbers. Goodrite, Vultol, trichloro-melamine, and Retarder W are suggested for heat-damaged stocks of GR-S, nitriles, and natural rubber.

Heat-damaged stocks do not appear to regain storage stability when diluted with noncuring master-batches and, when included in a fresh compound, seriously impair the storage stability of the mixture.

G-7503(1-2)

Ford, Earl W. and L.V. Cooper.

A STUDY OF THE FACTORS AFFECTING THE WEATHERING OF RUBBER-LIKE MATERIALS. I. II.

India Rubber World 124:696-698,701; 125:55-60. September - October 1951.

A literature survey indicates that there is wide divergence of opinion as to the relative roles played by ozone, light, heat, and moisture on the weather checking of rubber, although recent literature emphasizes the role played by ozone. The results of this project indicated that ozone is the only weathering agent which alone could produce visible effects on stocks compounded from Hevea, GR-S, GR-M, and GR-I polymer formulations. The other factors caused variations in the rate of ozone attack, but did not, of themselves, produce visible deterioration during the test periods.

A 60-station weathering apparatus having considerable flexibility is described. Rubber strips are exposed to controlled test conditions under static and dynamic elongations. The ozone concentration is independently and continuously controllable from 0.05 to 4,500 ppm or even higher. The temperature can be controlled between -40 and +100 C and the humidity from 0 to 100% RH at any test temperature. A system of lights and filters makes possible complete coverage of the entire light spectrum from 2,200A to 8,000A in bands approximately 500A wide. The system offers the advantages of cleanliness, in a compact source, high intensity and freedom from excessive heat radiation. Operating and replacement costs are relatively low.

Some typical results are given on the reproducibility of test data, comparison of the weathering of various polymer formulations, the effects of ozone, elongation, temperature, light, and humidity.

Butyl and neoprene stocks, in gum, black-loaded, and white formulations, were found to have extremely high ozone resistance. Neoprene stocks were somewhat less ozone resistant than butyl stocks. Hevea stocks were slightly better than similar GR-S stocks, but both were much inferior to neoprene. In the absence of ozone, light alone was found to produce little effect. Light treatment previous to or concurrent with ozone exposure slightly reduced the effects of ozone attack.

G-7625

Weinstock, K.V., L.M. Baker, and D.H. Jones.

RECENT DEVELOPMENTS IN THE FIELD OF OIL-ENRICHED RUBBERS.

Rubber Age (N.Y.) 70:333-338. December 1951.

High Mooney viscosity rubbers extended with low-cost petroleum softeners have been in production for more than a year and are being accepted as a replacement for GR-S or cold rubber. More than 50,000,000 lb of the polymers have been produced in the United States and Canada. Processing is similar to standard cold GR-S during all operations.

Tread wear performance in passenger tires is at least 10% better than standard cold rubber. Tread cracking resistance has been satisfactory in passenger tires, but early truck tire tests showed considerable tread cracking and tread separation. Improved compounds and construction methods have resulted in improved truck tire performance.

These oil-enriched rubbers are at least equal to regular cold rubber in weather- and ozone-cracking resistance. Some reported weather checking has probably resulted from a deficiency of anti-oxidant. Santoflex AW has been found to be particularly effective in minimizing this problem. In an aging test of 7 days at 212 F, oil-enriched rubber showed 117% tread wear and a crack total of 27 in., compared to 100% wear and 48 in. crack total for cold rubber.

In compounding, the balance among Mooney level of the rubber, oil content, and pigment loading is of the utmost importance. A direct relationship exists between Mooney level of the polymer and quantity of oil necessary for satisfactory processibility.

Careful selection of plasticizers results in low-temperature properties equal to those of polybutadiene rubbers. A RB-10 high Mooney rubber tested at -8 F showed a Shore durometer hardness of 62 and a Bashore rebound value of 17% compared to 78 and 5%, respectively, for a cold rubber tread stock, and 65 and 10%, respectively, for a natural rubber tread stock.

Extensive passenger tire tests indicate that in carcass compounds the new rubbers are superior to GR-S. Reported failures in large truck tires are due to tread separation or tread cracking and not to carcass deterioration. New and improved adhesives for both tread and carcass adhesion now permit better carcass evaluation.

G-7668

ATMOSPHERIC OR OZONE ATTACK; SHORT REVIEW OF THE LITERATURE.
India Rubber J. 121:220,222. August 1951.

G-7706

Morris, Ross E. and Joseph W. Hollister.
PLASTICIZERS FOR GR-S GASKET STOCKS TO BE USED AT LOW TEMPERATURES.
Rubber Age (N.Y.) 70:195-203. November 1951.

To select the best available plasticizers for use in a GR-S soft gasket stock for service at temperatures as low as -35 F, vulcanizates containing 181 plasticizers were tested for cold compression set; this property correlates with sealing ability of a gasket at low temperatures. The plasticizers are tabulated into groups, each group representing a 5% increase of vulcanizate compression set over the preceding group. Shore A hardness, Bashore rebound and specific gravity, all at 82 F, are also tabulated for each vulcanizate. A vulcanizate with no plasticizer had a compression set of 51.3%, and the control with Flexol TOF(tris(2-ethylhexyl)phosphate) fell within the range 28-35%. With the exception of TP-98, bis(methoxyethoxyethyl) adipate, the fifteen adipates tested were outstanding plasticizers, as shown by cold compression sets of less than 40% for the respective vulcanizates. Five of the twelve sebacates tested also yielded stocks with sets of less than 40%.

Thirty-five of the plasticizers which were outstanding for cold compression set were also tested for volatility and water extractability. The control stock without plasticizers showed a heat loss of 0.5%, whereas all the others exceeded this value. Five stocks, four of them containing low molecular weight adipates, decreased in molecular weight by amounts approaching 12.5%, which corresponds to complete loss of plasticizers. About one-third of the stocks had reasonable heat-loss values of less than 2%. The stock without plasticizer lost no material by water extraction and the majority of plasticized stocks lost less than 1%. Some plasticizers of supposedly identical chemical composition differed widely in volatility and extractability, owing probably to differences in purity.

The following nine plasticizers were selected on the basis of compression set at -35 F, volatility, and extractability as being outstanding for compounding in GR-S stocks: bis(2-ethylhexyl) and bis(2-butoxyethyl) adipates; bis(2-ethylbutyl) and bis(2-ethylhexyl) azelates; di-n-octyl phthalate; dicapryl, dihexyl, dioctyl, and di-iso-octyl sebacates. The control stock, containing Flexol TOF, cured fastest, 19 min, and had somewhat higher strength, 1310 psi, and ultimate elongation, 460%, than did the other stocks; its modulus at 300% elongation was 760 psi. Stock without plasticizer also cured in 19 min and had a tensile strength of 1600 psi, ultimate elongation of 340% and a modulus of 1360 psi at 300% elongation. Curing times at 310 F for the other stocks ranged from 26 to 31 min, tensile strength ranged from 1040 to 1220 psi, ultimate elongation ranged from 370 to 430%, and modulus at 300% elongation ranged from 710 to 800 psi.

All of the stocks tended to recover from compression even at -60 F. The relative benefit of the plasticizers was not the same at the different temperatures. Stocks were tested for recovery from compression set at 30° intervals from -60 to 30 F after recovery periods of 10 to 100,000 sec at each temperature.

G-7832

Allison, A.R. and I.J. Stanley.

OZONE DETERIORATION OF ELASTOMERIC MATERIALS; PRELIMINARY RESULTS OF A STUDY BY INFRARED SPECTROSCOPY.

Anal. Chem. 24:630-635. April 1952.

G-7845

Cuthbertson, G.R. and D.D. Dunnom.

CRACKING OF RUBBER AND GR-S IN OZONE; EFFECTS OF TEMPERATURE AND ELONGATION.

Ind. Eng. Chem. 44:834-837. April 1952.

Natural rubber exposed to a constant ozone concentration for 4 hr cracked at lower temperatures and elongations than either standard GR-S or low-temperature GR-S rubber. For each test temperature there existed an elongation below which no rubber specimen cracked; this was termed the 'cracking threshold'. The cracking threshold decreased with increasing temperature. The relationship between threshold and temperature appears to be qualitatively the same for all three polymers. A possible explanation for the relationship, on the basis of ozonide film strength and ozone stability with temperature, is suggested. Between 30-90 F, crack density increased and crack size decreased with increasing elongation.

Rubber compounds similar to those used in tire treads or side-walls were simplified for these tests; the antioxidant was omitted. One-in. wide strips of the test compounds were cut from tensile slabs which had been cured for 45 min at 292 F. Strips were stretched to the desired elongation at room temperature and placed in an ozone test chamber. They were conditioned at the test temperature (-10, 10, 30, 50, 70, and 90 F $\pm$ 2 F) for at least 1 hr, then were exposed to an ozone concentration of 1.4 ± 0.1 ppm for 4 hr at each temperature. Prints from the exposed samples were made by inking the sample surface and taking an impression on paper.

G-7847

Popp, George E. and Lynn Harbison.
OZONE AND SUNLIGHT EFFECT ON AGING OF CARBON BLACK VULCANIZATES.
Ind. Eng. Chem. 44:837-840. April 1952.

Carbon blacks, regardless of type, particle size, structure, and physical properties which they impart to rubber, do not affect the rate or the degree of checking and cracking of natural and synthetic rubber vulcanizates exposed to ozone or sunlight under static stress. Natural rubber withstands such exposure for much longer periods than does the X-478 synthetic low-temperature polymer studied. The degree of ozone and weather damage is more pronounced when an effective antioxidant is not used in the rubber compound. Four antioxidants were tested: Rubber containing nickel dibutyldithiocarbamate performed best and showed only minor surface checking. Rubber containing Santoflex AW, a p-phenetidine derivative, exhibited mild checking and slight ozone cracking, but was better than rubber containing either BLE resin—a diphenylamine product—or Helizone—a mixture of waxy materials.

Samples 6 by 0.5 in. were prepared from ASTM tensile test sheets of natural rubber cured 40, 60, or 90 min at 280 F, and of a low-temperature polymer, X-478, cured at 41 F. Formulations with and without antioxidants were made using HAF, EPC, MAF, HMF, and SNF type carbon blacks. One series of specimens was exposed under 12.5% elongation, another similar series was bent 180° prior to exposure. Weathering tests were conducted in Akron, Ohio starting in April and terminating after 32 days for synthetic rubber and 63 days for natural rubber vulcanizates. In ozone aging tests, synthetic rubber samples were exposed in an ozone box for 8-12 hr and natural rubber was exposed for 132 hr.

G-7848

Bartel, A.W. and J.W. Temple.
OZONE IN LOS ANGELES AND SURROUNDING AREAS.
Ind. Eng. Chem. 44:857-861. April 1952.

G-7849

Winkelmann, H.A.

STATIC EXPOSURE TESTING OF AUTOMOTIVE COMPOUNDS.

Ind. Eng. Chem. 44:841-850. April 1952.

The factors that influence the resistance of rubber products to ozone were studied in various outdoor and laboratory exposures. Manufacturing variables which influence resistance are selection of polymers, preparation of master batches, degree of purity, degree of dispersion, selection of wax and dispersing agent, aging of mixed and prepared stock before curing, cure and degree of flow during cure, method of molding, and type of lubricant. Exposure variables include local and seasonal changes in ozone concentration, temperature, sunlight, and humidity, and degree of test sample distortion. Because of these weathering factors and their interactions, many tests and intelligent judgment are required for correlating results of accelerated and natural exposures. Many compounds that perform well in the ozone chamber prove unsatisfactory in outdoor weathering, and vice versa.

Rubber cured or molded under strain cracks faster than when cured or molded at rest; the greater the strain the faster the rate of cracking. Aging of uncured or extruded stock before molding decreases cracking. Aged, uncured stock cured under strain cracks slower than unaged, strain-cured stock. Uncured stock aged 24 hr performed well, whereas stock aged 4 hr or less prior to cure cracked on static exposure.

A longer aging period before exposure is beneficial for medium quality compounds. Regardless of the method of molding or curing, natural rubber and GR-S samples performed equally well when aged 48 hr prior to exposure at Miami and Chicago and in a Pontiac ozone box, but GR-S cracked less in a Crabtree-Kemp ozone chamber. Heating 15 min at 158 F before exposure in this chamber decreased cracking of injection- and compression-molded natural rubber, but increased the cracking of extruded natural rubber and of injection- and compression-molded GR-S; it had no effect on transfer-molded natural and GR-S rubbers or on extruded GR-S. Heating for 2 hr prior to exposure was harmful.

Weathering behavior can frequently be predicted from microscopic observations of the rubber compounds; the better they are dispersed the better they perform on exposure. Presence of grit, pigment, agglomerates, flocculations, and foreign matter in general, as well as manufacturing defects such as blisters and air traps are detrimental to weather resistance. Of ten commercial dispersing agents added in 1, 3, and 5 parts to 100 parts GR-S, only Marasperse CB showed no effect in Florida and Chicago exposure tests; Lomar PW and Indulin C were satisfactory at Chicago. Other agents, such as Triton R-100 and Masenoid D, used to make carbon black slurries for the GR-S master batches increased cracking.

Low-melting microcrystalline waxes apparently imparted a more protective wax bloom than higher-melting fractions. Blending microcrystalline waxes with paraffin improved weather aging. High melting point paraffins seemed superior to lower melting fractions in the more severe Florida exposure, although no such difference was noted at Chicago. Longer cures (20 min) generally caused faster bloom development than short (5 min) cures, but after shelf-aging the short-cure rubber developed a heavier bloom than the long-cure rubber.

Of several pyrrole type compounds, NBC (du Pont) is recommended for ozone protection of GR-S but not for natural rubber.

Metal salts such as manganous, ferrous, and ferric sulfates and copper stearate, which are usually present in rubber compounding ingredients, increased the cracking of GR-S and natural rubber during 60 days' weathering at Miami when added in 0.0005-0.05 parts per 100 parts rubber; most of these concentrations accelerated cracking after 22 days at Chicago, but after 220 days all samples were as good as or better than the untreated controls. Similarly, cracking in the ozone chamber at 100 F was initially accelerated by the presence of these salts (except manganese), but after 70 hr all samples rated as well as salt-free controls. Copper, manganese, and iron naphthenates, in similar concentrations, did not affect the performance of rubber and GR-S after 48 days at Chicago, but the manganese salt accelerated cracking of natural rubber, and the iron salt increased that of both natural rubber and GR-S during 30 days at Miami.

Neoprene showed better weather resistance than GR-S or natural rubber when similarly loaded with carbon black. The compound should contain at least 50% neoprene by volume, using clay as an optimum mineral filler. Whiting and partial substitution of GR-S or natural rubber for neoprene impaired the aging behavior.

Butyl rubber properly compounded and wax-protected, and reclaimed Butyl mixed GR-S by special techniques showed good weather-aging.

G-7928

Rugg, John S.

OZONE CRACK DEPTH ANALYSIS FOR RUBBER.

Anal. Chem. 24:818-821. May 1952.

The increase of crack depth in rubber exposed to ozone is proportional to the total crack growth and furnishes a reliable criterion for the quantitative assessment of ozone damage, whether as a function of weathering factors or of compounding variables. This relationship is the basis for a convenient analytical test which requires little more than a twentyfold magnifying microscope and is practically independent of human judgment.

A cracked, relaxed rubber sample, cross-sectioned vertical to the length of the cracks, is scanned with the microscope; the deepest crack and those within 10% of the deepest are measured on a millimeter scale in the field and the results averaged. Reproducibility on replicate samples is ± 0.05 mm.

Quantitative results obtained by this method on natural rubber specimens confirm and supplement previously reported qualitative trends. Thus, quantitative data are presented graphically for the increase of crack depth with exposure time and with ozone concentration; the decrease of crack depth with percent elongation; the relationship between crack depth and crack distribution; the effects of constant load v. constant deflection; and correlations between natural weathering and accelerated ozone testing.

G-7929

Thompson, D.C., R.H. Baker, and R.W. Brownlow.
OZONE RESISTANCE OF NEOPRENE VULCANIZATES; EFFECT OF COMPOUNDING
INGREDIENTS.
Ind. Eng. Chem. 44:850-856. April 1952.

The effects of compounding factors on the resistance of neoprene vulcanizates to accelerated ozone attack were studied. Neither the presence of accelerators nor their influence on the modulus of fully cured neoprene vulcanizates affected ozone resistance. At 300% elongation, corresponding to a stress of 1150-2275 psi, however, the lower modulus stocks were more ozone resistant.

The addition of fillers, including carbon blacks, clay, natural whiting, calcium and magnesium carbonates, calcium silicate, barytes, asbestene, and blends of natural whiting and clay, impaired ozone resistance in proportion to the amount added. The coarse particle size fillers were particularly harmful.

Petroleum-base plasticizers had a negligible adverse effect, but several esters such as dibutyl sebacate, and similar types of plasticizers were significantly harmful. Certain unsaturated vegetable oils, notably linseed, tung, castor, menhaden, soybean, cottonseed, and corn oils, in decreasing order of merit, enhanced the ozone resistance of neoprene vulcanizates. Peanut oil did not give any improvement, and coconut oil had a serious adverse effect. Esters derived from castor oil, such as butylacetyl ricinoleate, gave approximately the same results as the oil itself, but methylacetyl ricinoleate imparted less ozone resistance.

Commonly used softeners, extenders, and tackifiers, such as mineral rubber, coumarone-indene and butadiene-styrene resins, and various factices derived from soybean, rapeseed, and castor oils, showed no apparent effects on ozone resistance. If materials of these kinds do provide ozone resistance, it is only by virtue of the stress relaxation they induce in vulcanizates. Wood rosin, however, provided an exceptional degree of resistance to ozone.

A number of antioxidants, especially those which reduce flex cracking, also act as ozone-resisting agents in neoprene vulcanizates. Their efficiency is profoundly influenced by the amount used and the concentration of ozone during exposure. Of twenty antioxidants tested under equal conditions, diphenyl-p-phenylenediamine (DPPD) and di-p-methoxydiphenylamine (Thermoflex) provided the highest degree of ozone resistance when used in amounts greater than 1% based on the neoprene. Certain nondiscoloring-type antioxidants such as p-phenylphenol were harmful to ozone resistance. The presence of wax such as Heliozone reinforced the difference between antioxidants actions.

Exceptional resistance to high ozone concentrations, viz., 144-hr exposure without cracking, was shown by a typical neoprene cable-jacket compound having the following formula: 100 parts neoprene type GN-A; 1.25 each of DPPD and Thermoflex; 2.5 phenyl-2-naphthylamine; 5 phenyl-1-naphthylamine; 0.5 stearic acid; 4 magnesia; 25 EPC carbon black; 50 hard clay; 10 light process oil; 5 Heliozone; 10 zinc oxide; and 0.5 Permalux.

PDC Comment: Related information from the same source has been abstracted in an earlier volume of PDA. [DuPont de Nemours and Co. EFFECT OF COMPOUNDING ON OZONE RESISTANCE OF NEOPRENE VULCANIZATES. Bulletin BL-238. September 1950. PDA 9: Plus 89, C-1051].

G-8017

McKinley, R.B. and C.H. Seaberg.
MOISTURE VS. RUBBER INSULATION.
Gen. Elec. Rev. 55(4):56-60. July 1952.

Electrical measurements made on rubber insulation immersed in water 252 wk at 40 C showed that the only acceptable short-term test that reliably predicts long-term insulation performance is gravimetric water absorption. This is expressed as milligrams of water absorbed per square inch of surface immersed in water for 7 days at 70 C. For satisfactory service performance in wet locations, the insulation should absorb not more than 10 mg per sq in. in the 7 days. Changes in specific inductive capacity (dielectric constant) or power factor after 2 wk in water at 50 C do not permit reliable predictions of long-term performance. The exposure period is too short to show what effect moisture absorption will have on the electrical properties of the insulation.

Rubber insulations used for the long-term tests included three synthetic rubbers, viz., polyvinyl chloride, Buna-S, and an ozone-resistant Butyl compound. Eight natural rubber formulations were also used, viz., three ozone-resistant oil-base compounds, two 30% rubber compounds, a 60% submarine-type deproteinized insulation, a 35% heat-resistant, and a 35% moisture- and heat-resistant compound. All insulation was 7/64-in. thick on No. 8 Awg wire. Some samples were immersed with no applied current or voltage; others had 1,500 v applied between the conductor and water, but no current; while still others had 60 cycles applied, but no voltage. Periodic readings were taken of specific inductive capacity and power factor at 40 and 80 v per mil.

With the exception of the 60% submarine insulation and two of the oil-based types, current through the conductor prolonged the life of most installations. Voltage accelerated moisture absorption, with consequent shorter insulation life. Absence of either voltage or current resulted in intermediate insulation life. Insulation designed for exceptional moisture resistance outlasted ordinary types. Inclusion of antioxidants and organic accelerators prolonged the life of an insulation when the cable carried current. The combination of good heat- and moisture-resisting properties proved ideal for power cables.

Buna S and Butyl types compounded similarly to natural rubber for good moisture- and heat-resistance make excellent insulation. Butyl rubber is especially recommended for circuits rated at more than 2,000 v. For power cable applications such as underground feeders and secondary network cable, the 35% moisture- and heat-resisting compound is best. The logical choice for communication circuits is 60% submarine compound. Polyethylene is also satisfactory for this purpose when a thermoplastic insulation is not objectionable. A moisture-resisting polyvinyl chloride compound is suggested for control and signal circuits because it combines excellent moisture resistance with flame, oxidation, and chemical resistance.

G-8161(11)

Battelle Memorial Institute, Columbus, Ohio.
STUDY OF OUTDOOR NATURAL AGING AND WEATHERING OF ORGANIC MATERIALS,
by C.W. Hamilton and others.
Final Report; U.S. Dept. of the Army. Signal Corps.
Contract No. DA-36-039 SC-15436. June 1954.

Attempts were made to correlate natural outdoor aging processes of plastic cable jacketing materials with those occurring under accelerated aging conditions in the laboratory. Materials studied included four kinds of nylon, GR-S, perbunan-vinyl, and compounded polyvinyl chloride. Each of these materials was exposed in the form of WD-1 infantry field wire, 5-pair cable, Spiral-4 cable, filament, sheet, slabs, and tubing.

The approximate service life of each type of wire and cable at each location was determined by the length of exposure before a sample failed the low-temperature (-40 C) mandrel-wrap test. By comparing the rate of change of physical properties of the other specimens with the service-life ratings of the wire and cables, certain relationships between service life and physical properties such as tensile strength and electrical conductivity were found. Changes in tensile strength occurring over several months of outdoor exposure could be duplicated in nylon filaments by a few days' aging in a circulating-air oven at 140 C. Similar changes also were produced by X-irradiation.

With the possible exception of perbunan-vinyl, which failed after 6-9 mo, all cable materials tested were resistant to weathering. Judging from the mandrel-wrap test, the four types of nylon deteriorated in the same relative order regardless of exposure site, Type FM-3606 being the most resistant and FM-7001 the least resistant to aging, with Types FE-2103 and FE-1085 intermediate. FM-3606 lasted 9 mo in the Canal Zone, 12 mo in Florida, Arizona, and Ohio, and over 18 mo in Canada when tested on WD-1 wire. For FM-7001, the respective values were 2, 1, and 3 mo only. The same order of merit was established on nylon filaments exposed outdoors unshaded, using tensile strength as the criterion. The relative severity of the five exposure stations decreased in the order Ohio, Arizona, Canal Zone, Florida, and Canada, indicating that industrial pollution was a more important factor than relative humidity. Among the rural stations, daily maximum temperature was the decisive factor, supported by the interaction of light and humidity. To obtain an age-resistant nylon, a heat stabilizer plus an ultraviolet screener such as carbon black must be incorporated.

PDC Comment: All quarterly progress reports except Part 4 are on file at the Center. [321 p. February 1952 - April 1954.
PDC G-8161(1-3,5-10)].

G-8469(2)

Gardner, E.R. and N.J. Berridge.
THE DETERIORATION OF MILKING RUBBERS. II. THE EFFECT OF FAT.
J. Dairy Research 19(1):31-38. February 1952.

G-8479

CHLOROSULFONATED POLYTHENE ELASTOMER COMBINES DURABILITY WITH
UNLIMITED COLOR POSSIBILITIES.
Chem. Processing 15(9):18-19. September 1952.

G-8774

Creed, K.E., jr., R.B. Hill, and J.W. Breed.
EVALUATION OF OZONE PROTECTIVE AGENTS FOR ELASTOMERS; APPARATUS
FOR THE EVALUATION UNDER DYNAMIC CONDITIONS.
Anal. Chem. 25:241-244. February 1953.

A newly developed dynamic apparatus provides a more effective means for accelerated evaluation of ozone protective agents in synthetic elastomers than the tentative ASTM method. It features a new mechanical arrangement for flexing the rubber, a new specimen shape, rigid control of ozone concentration, and a new rating system. The apparatus consists of a series of rotating pulleys within a circular chamber. The test specimens, circular molded belts, are rotated around two pulleys which gives them approximately 75 flexes per min with an elongation of from 0 to 20%. The flexing provides a mobile surface, so that rigid waxy films cannot be formed. Use of molded specimens eliminates the possibility of freak cracking and anomalies due to minute nicks or imperfections during dieing out. The larger surface available for examination facilitates interpretation of results. Air passes through the chamber at a rate of 1 cu m per hr with a controlled ozone concentration of 0.25 ± 0.05 ppm at 30 C. Uniformity is insured by use of a fan in the chamber. The concentration of ozone is determined by the potassium iodide method. By a simplified rating system, a nontechnical person can rate a large number of specimens rapidly and without elaborate equipment.

G-8823(1)

Leigh-Dugmore, C.H.
THE OZONE CRACKING OF RUBBER.
Rubber Age and Synthetics 33:398-399. November 1952.

G-8934

Kirshenbaum, A.D., A.G. Streng, and A.H. Nellen.
A STUDY OF THE OXIDATION OF RUBBER BY MEANS OF THE ISOTOPIC METHOD.
Rubber Age (N.Y.) 72:625-630. February 1953.

Using heavy oxygen (O^{18}) as tracer, the isotope-dilution method of analysis was employed to determine the oxygen content of smoked sheet rubbers passed through the plasticator, exposed to ozone, and oxidized in the Geer oven and in the oxygen bomb. The oxygen values obtained agreed to within $\pm 0.18\%$ with those determined by weight gain.

Oxygen-bomb data showed a gradual increase in the oxygen content of the rubber during the first 30 hr of oxidation at 70 C, but no further increase when oxidation was prolonged for another 100 hr. This indicated that all the double bonds and oxidizable chain terminals were oxidized during the first 30 hr. Additional oxidation beyond 130 hr caused molecular degradation and subsequent oxidation of the split rubber molecules, as shown by the softening of the rubber and by a further increase in oxygen content.

The oxygen content of rubber also increased on passing through a plasticator, ozonation, and heating for 18 days in a Geer oven at 105 C. The oxygen content decreased on degassing, indicating the removal of oxygen-containing substances. Analysis of the products showed that, apart from traces of carbon monoxide and dioxide, water was the only constituent removed from the rubber.

G-9168

Fisher, Harry L.
LATEST DEVELOPMENTS IN SYNTHETIC ELASTOMERS.
India Rubber World 127:641-645,712. February 1953.

G-9396(3)

Augustana Research Foundation, Rock Island, Ill.
STUDY OF REACTION OF OZONE WITH POLYBUTADIENE RUBBERS.
Report No. 3; U.S. Ordnance Corps. Contract No. DA-11-022-ORD-329.
February 1953.

The amount of ozone absorbed by standard vulcanized GR-S rubber in the static state decreases gradually until the ozone-air stream reaches its original value. This indicates that ozone attack on rubber is a surface reaction which gradually causes the formation of a protective coating that greatly, if not completely, retards further attack if the sample is relaxed. This coating probably contains ozonization products of the rubber polymer and of the ozone-sensitive components added to the rubber or formed during vulcanization.

Standard vulcanized GR-S rubber containing an antioxidant usually absorbs greater amounts of ozone than does the uninhibited standard vulcanizate. If the antioxidant is efficient, the ozone-air stream does not return to its original value. In these tests a small, nearly constant, amount of ozone is continually absorbed for a long time. If this amount—the 'residual ozone absorption'—is greater than the atmospheric ozone concentration, the antioxidant is a good one for rubber both in the relaxed state and under static stress.

The presence of hydrocarbon wax in rubber containing an antioxidant is beneficial in two ways. It greatly improves the resistance of rubber to ozone attack, since it increases the residual ozone absorption. Moreover, hydrocarbon wax increases the value of antioxidants, making fair inhibitors good ones, probably by facilitating their migration to the rubber surface through a possible swelling of the rubber, solvent or lubricating action. Inhibitors such as N,N'-di-sec-butyl-p-phenylenediamine and certain liquid alkyl and alkoxy derivatives also cause the rubber to swell and thereby reach the surface at such a rate that the residual ozone absorption rate is high enough to protect the rubber without the addition of wax.

The fact that one inhibitor absorbs a greater amount of ozone than another does not necessarily make it a better protective agent. The factor that determines the value of a compound as an antioxidant for vulcanized GR-S rubber is the constancy of the residual ozone absorption rate.

G-9396(4) Augustana Research Foundation, Rock Island, Ill.
STUDY OF REACTION OF OZONE WITH POLYBUTADIENE RUBBERS.
Report No. 4; U.S. Ordnance Corps. Contract No. DA-11-022-ORD-329.
July 1953.

G-9396(5) Augustana Research Foundation, Rock Island, Ill.
STUDY OF REACTION OF OZONE WITH POLYBUTADIENE RUBBERS.
Report No. 5; U.S. Ordnance Corps. Contract No. DA-11-022-ORD-329.
February 1954.

The ozone absorption by GR-S rubber rods of a given age under dynamic stress is somewhat greater than under static stress at the same temperature and ozone concentration. Ozone absorption may increase with the severity of dynamic stress.

The ozone absorption of an aged GR-S rubber rod was about 1.5 times as great but the time to the first ozone cracks was 2.5 times as long as for a freshly molded sample of the same stock. These results may be due to a slow migration of the antioxidants to the rubber surface. In a standard GR-S rubber rod containing 5.4 parts N,N'-di-sec-butylbenzidine but no wax, under 20% elongation plus cyclic stress of 1.15 cm every 15 sec for 24 hr, the rate of antioxidant migration in an ozone atmosphere was only 12% that in a statically-stressed standard GR-S rubber rod containing 1 part Heliozone wax. This lower rate of migration was not sufficient to prevent ozone attack. Under both experimental conditions, however, the rate of ozone absorption by N,N'-di-sec-butylbenzidine followed a pseudo first-order reaction.

PDC Comment: An earlier progress report of this project was abstracted previously. [Report No. 3; U.S. Ordnance Corps. Contract No. DA-11-022-ORD-329. February 1953. PDA 11: Plas 133, G-9396(3)].

G-9396(6) Augustana Research Foundation, Rock Island, Ill.
STUDY OF REACTION OF OZONE WITH POLYBUTADIENE RUBBERS.
Report No. 6; U.S. Ordnance Corps. Contract No. DA-11-022-ORD-329.
July 1954.

G-9423 Winkelmann, H.A.
CORRELATION OF OZONE CHAMBER TESTS WITH OUTDOOR EXPOSURES.
Sheller Manufacturing Corp. September 1953. [2] 1.

G-9789 Crabtree, James and B.S. Biggs.
CRACKING OF STRESSED RUBBER BY FREE RADICALS.
J. Polymer Sci. 11:280-281. September 1953.

Cracking, indistinguishable from that produced by ozone, was found in stressed rubber exposed to vapors of volatile peroxides irradiated by ultraviolet light. Because the presence of oxygen was not necessary, the reaction occurring equally well in nitrogen, cracking of this kind is apparently caused by free radicals

resulting from the photolysis of the peroxides. In the presence of nitrogen peroxide the reaction was accelerated as shown by an increase in the rate of cracking and by the peroxide balance obtained from chemical analysis. Since no change occurred in the dark, the photolyzed nitrogen peroxide evidently functions as a catalyst for the breakdown of the volatile peroxide. Cracking was observed by radicals such as tert-butoxy, phenyl, benzoyl, acetyl, and hydroxyl.

This laboratory observation suggests that a similar mechanism may contribute to the cracking of rubber under industrial atmospheric conditions such as are present in the Los Angeles smog area, the free radicals being produced by the catalyzed photolysis of volatile peroxides present in the smog. The suggested mechanism is that nitrogen peroxide acts as a catalyst for ozone formation through photolysis by sunlight with liberation of atomic oxygen and nitric oxide, followed by ozone formation from oxygen, and recombination of nitric oxide with molecular oxygen to restore the nitrogen peroxide.

G-9889

Smith, Doreen M. and V.E. Gough.

OZONE CRACKING: A CINEMATOGRAPHIC STUDY.

Trans. Inst. Rubber Ind. 29:219-237. October 1953.

The development of cracks in stretched rubber exposed to ozone was studied by a technique of time-lapse cinemicrography. Every 12 sec, a 16-mm cine-camera with a half-open shutter and geared to a synchronous motor takes a 3-sec picture of a 6-12 sq mm central area of a specimen stretched behind the glass window of an ozone chamber. Film projections of crack formation and development at 30, 15, and 7 1/2% strain were analyzed. In addition to giving a dynamic picture of the formation and growth of cracks, this film technique permits making detailed measurements throughout the cracking process.

Formation and growth are the two main phases in the cracking of strained rubber by ozone. Crack formation is statistical in character, the rates being normally distributed with respect to the logarithm of time and the crack location being random. Rate of crack growth is constant in time except when it is modified by crack joining or stress release owing to the presence of neighboring cracks.

In an attempt to co-ordinate these facts with the known effects of stress and to explain the discrepancy between the high number of available double bonds and the relatively low number of observed cracks, it is suggested that visible cracks commence only when several adjacent molecules carry the applied stress and when neighboring double bonds in these molecules are simultaneously attacked by ozone. This theory explains the relatively few visible cracks, and is in agreement with observed facts, e.g., the increase of crack density with increasing temperature.

G-10016(1)

Case Institute of Technology, Cleveland, Ohio. Dept. of
Chemistry and Chemical Engineering.
RESEARCH ON OXIDATION AND AGING OF NATURAL AND SYNTHETIC RUBBER,
submitted by J. Reid Shelton, William L. Cox, and
William T. Wickham.
Technical Report No. 1; U.S. Ordnance Corps. Contract No.
DA33-019-ORD-1207. July 1953.

The oxidation and aging behavior of natural and synthetic rubber stocks containing varying concentrations of typical amine and phenolic-type antioxidants was studied. In particular, the relationship between oxygen absorption and deterioration of properties was determined to see if the catalytic effect of excess antioxidant on the rate of oxidation is reflected in a corresponding increase in the rate of deterioration of physical properties.

The conventional 0.125% concentration of PBNA (phenyl-2-naphthylamine) in GR-S black stock proved to be optimum for maximum rate of oxygen absorption. As measured by changes in properties, the small amount of additional oxygen absorbed with higher PBNA concentrations was not particularly harmful. Higher concentrations were actually beneficial in that stiffening was less, as evidenced by a smaller modulus increase. The optimum concentration of PBNA in Hevea black stock was 2%. The additional oxygen absorbed was equally effective in the degradation of properties, both tensile and modulus.

The differences in the effects of PBNA on aged properties of GR-S and Hevea black stocks may be explained by differences in chain structure and in the nature of the reactions involved. To the extent that radicals derived from the antioxidant replace an equivalent concentration of radicals such as $R\cdot$, $RO\cdot$, and $RO_2\cdot$, all degradation reactions are diminished. The net effect upon physical properties depends upon whether chain scission or crosslinking is predominant. Crosslinking predominates in GR-S, probably because the side-chain vinyl groups are more susceptible to addition of free radicals than are internal double bonds. Chain scission is usually the predominant reaction in Hevea stocks, as reflected in reduced tensile and modulus values. Thus, added antioxidant produces less hardening in GR-S and less softening in natural rubber.

The net effect of excess antioxidant (beyond the optimum for rate of oxygen absorption) on the physical properties of rubber may be either increased or decreased deterioration, depending upon which of the opposing tendencies predominates. If the additional oxygen is used up by attack on the antioxidant, no direct effect on properties results. If, however, the attack of oxygen on excess antioxidant produces chain-initiating radicals which increase the rate of formation of $R\cdot$, $RO\cdot$, and $RO_2\cdot$ radicals more than the rate of removal is increased by reaction of these radicals with the additional antioxidant and antioxidant radicals, the net effect is a corresponding increase in deterioration of physical properties. Such an effect was observed with an excess of PBNA in natural rubber.

Tenamene 2 (N,N'-di-sec-butyl-p-phenylenediamine) had only a slight effect on the rate of oxygen absorption of Hevea black stock, although the inhibited stocks retained their properties on aging much better than did the uninhibited control stock. Oxygen consumed by reaction with the antioxidant accounts partly for the observed

behavior. Another possible explanation is that for a given total radical concentration (as evidenced by nearly the same oxygen-absorption rate), the presence of antioxidant radicals would mean a corresponding decrease in the usual carbon and oxy radicals which are normally involved in both chain scission and cross-linking. This interpretation offers a possible explanation of the phenomenon called the 'deactivating effect'.

Hydroquinone gave a maximum reduction in rate of oxidation of 1% concentration. The decrease in tensile strength for a given absorption of oxygen was comparable for three different concentrations. The modulus was progressively higher at the higher concentrations, suggesting that hydroquinone may promote some type of crosslinking or possible decrease scission, as did PBNA. The optimum concentration of Deenax (2,6-di-tert-butyl-p-cresol) in the Hevea black stock was 3%, both from the standpoint of rate of oxidation and deterioration of properties during aging. The rate of change in properties was generally proportional to the oxygen absorbed.

A comparison of the change in tensile strength for the optimum concentrations of four antioxidants in Hevea black stocks as a function of the amount of oxygen absorbed showed that the phenols follow one curve and the amines another.

For a given absorption of oxygen, the tensile strength of the amine-inhibited black stocks changed somewhat less than did the phenolic-inhibited stocks.

This study showed also that although oxygen-absorption data usually make it possible to select the best prospects in a comparative study of antioxidants, it is also important to measure changes in physical properties. In most cases, changes in properties are in proportion to oxygen absorbed, but there are some exceptions in which the degradation reactions are altered without a corresponding change in the overall rate of oxidation.

G-10016(2)

Case Institute of Technology, Cleveland, Ohio. Dept. of Chemistry and Chemical Engineering.
RESEARCH ON OXIDATION AND AGING OF NATURAL AND SYNTHETIC RUBBER, submitted by J. Reid Shelton, William L. Cox, and William T. Wickham.
Status Report No. 2; U.S. Ordnance Corps. Contract No. DA-33-019-ORD-1207. September 1953.

G-10016(3)

Case Institute of Technology, Cleveland, Ohio. Dept. of Chemistry and Chemical Engineering.
RESEARCH ON OXIDATION AND AGING OF NATURAL AND SYNTHETIC RUBBER, submitted to Rock Island Arsenal by J. Reid Shelton, William L. Cox, and William T. Wickham.
Technical Report No. 2; U.S. Ordnance Corps. Contract No. DA33-019-ORD-1207. June 1953 - February 1954.

G-10254

Morris, Ross E. and Arthur E. Barrett.
EFFECT OF ARCTIC EXPOSURE ON HARDNESS OF ELASTOMER VULCANIZATES.
India Rubber World 129:773-775. March 1954.

Medium soft gasket stocks of natural and GR-S rubber and of neoprene GN, RT, and W vulcanizates were exposed from March 1950 to February 1952 to the arctic weather of Point Barrow, Alaska. Changes were followed by monthly hardness measurements made with a Rex gage.

The hardness of elastomer vulcanizates after 16-20 hr laboratory conditioning at low temperatures is not always the same as that attained in the Arctic. The difference is due to the prolonged periods of cold arctic weather which induce crystallization, whereas the short laboratory exposure is not sufficient to induce much crystallization. Laboratory hardness data indicate that both natural rubber stock and GR-S containing di-n-hexyl adipate are outstanding in retaining flexibility at low temperatures, whereas cold-compression-set values for natural rubber stock containing 0.75 part sulfur show some crystallization at -35 F which would be even greater on prolonged Arctic exposure at -40 F and even at -20 F.

GR-S proved to be more suitable for compounding stocks for Arctic use than did either natural rubber or the neoprenes. GR-S stock plasticized with di-n-hexyl adipate was outstanding in cold resistance, but even GR-S plasticized with Para Flux behaved better than natural rubber and neoprenes. Natural rubber containing 2.5 parts sulfur showed better low-temperature behavior than did stocks containing 0.75 part sulfur because sulfur crosslinks hinder crystallization. Among the neoprenes, type RT performed better than did type GN.

G-10281

Pollack, Louis R.
OXYGEN ABSORPTION VERSUS CONVENTIONAL AGING OF COMMERCIAL VULCANIZATES.
India Rubber World 130:53-57. April 1954.

Thirty-four commercial vulcanizates, including Hevea, GR-S, Chloroprene, and GR-N, were aged in the oxygen bomb, in the air oven, and by an oxygen-absorption test. Aging resistance in the bomb is evaluated more satisfactorily if physical property losses are measured only after the fourth day. Rate of loss of physical properties during the constant-rate stage should provide a better evaluation of aging resistance than does the total loss during the first two days. The total loss of physical properties between the fourth and the fourteenth day in the bomb may be used as a substitute for the rate of loss.

Oven testing of commercial vulcanizates fails to evaluate aging resistance alone, but measures the resultant of after-vulcanization and degradation effects. Furthermore, inordinate weight is given to the after-vulcanization effect.

Because of the nature of the chemical reactions involved, oxygen-absorption rate provides a more fundamental and rapid evaluation of the oxygen aging of a vulcanizate than do conventional tests.

G-10346

Helin, Arthur F.
 PROPERTIES OF LOW-STYRENE GR-S-PLASTICIZER BLENDS.
 Ind. Eng. Chem. 46:1730-1734. August 1954.

In an attempt to improve the low-temperature properties of GR-S rubber, 100 parts of a conventional low-temperature (41 F) butadiene-styrene (85/15 GR-S) latex of high Mooney viscosity were blended with 40 parts of various plasticizers by the technique developed for preparing polymer-oil master batches. The plasticizers included diisooctyl succinate and sebacate, diisobutyl adipate and azelate, bis(butoxyethyl) adipate, bis(2-ethylhexyl) azelate, dihexyl sebacate, dibutyl and di-n-octyl phthalates, an unspecified thiol ester (Flexol TWS), and tris(2-ethylhexyl) phosphate (alone or containing 25% Califlux GP processing oil). Stocks prepared by conventional recipes were evaluated by Gehman torsional stiffness, low-temperature compression set, and temperature retraction (TR).

None of the plasticizers produced a compound superior in tensile strength, cold flexibility, and freedom from crystallization at low temperatures. Masterbatches containing diisooctyl succinate, tris(2-ethylhexyl) phosphate, and bis(butoxyethyl) adipate showed the best balance of low-temperature properties. Stocks containing dibutyl phthalate, bis(butoxyethyl) adipate, and 75/25 tris(2-ethylhexyl) phosphate/Califlux GP offered the best compromise between good tensile properties at 212 F and good low-temperature performance.

G-10546

Shaw, Robert F., Z.T. Ossefort, and W.J. Touhey.
 ANTIOXIDANTS FOR GR-S RUBBER.
 Rubber World 130:636-642. August 1954.

Outdoor exposure and ozone cabinet tests of stressed GR-S vulcanizates showed that certain aromatic amines acted as antioxidants. These amines had the structure $(R-NH)_2A$ where R is hydrogen, phenyl, or alkyl up to 20 carbons, and A represents one, two, or three aromatic rings either joined together or separated by small groups such as CH_2 . Among these amines, 3-5 parts of the alkyl p-phenylenediamine type protected stressed GR-S vulcanizates up to 2 yr. The best antioxidants were those of intermediate molecular weight, such as N,N'-dioctyl-p-phenylenediamine, which represent a balance between the low vapor pressure plus slow migration of high molecular weight compounds and the high vapor pressure plus fast migration of low molecular weight compounds. The migration rate was increased by incorporating 1 part per hundred of wax. These amine antioxidants functioned also as antioxidants in GR-S on heat aging, but tended to lose their effectiveness in subsequent ozone exposure. Conventional general-purpose antioxidants of the amine type, such as Neozone D and AgeRite Resin D, enhanced the ozone resistance of the amine antioxidants.

GR-S polymers made at low reaction temperatures and with low styrene contents are the most susceptible to ozone cracking. Therefore, most of the tests were done on a 90/10 ratio butadiene/styrene copolymer made at 41 F. In all tests, absence of cracking was noted rather than measurement of length, width, or depth of cracks. Outdoor tests are difficult to correlate with accelerated ozone cabinet tests because of fluctuation of atmospheric ozone concentration. At

periods of lower ozone concentration the inhibitor has an opportunity to migrate to the surface and replenish the supply, a condition impossible in accelerated testing.

Further information, such as availability, toxicity, and staining of amine antioxidants, is required before commercial use becomes a reality.

PDC Comment: Abstracts of other reports on this subject from the Rock Island Arsenal may be found on pages Plas 170, Vol. 11 (PDA A-1245) and Plas 27 and 28, Vol. 12 (PDA A-1287, A-1286).

G-10584

Jaray, F.F. and A.E. Lever.
RESISTANT RUBBERS AND ELASTOMERS.
Corrosion Prevention and Control 1:477-481,484. October 1954.

G-10730

Delman, A.D., B.B. Simms, and A.R. Allison.
EVALUATION OF CHEMICAL PROTECTANTS AS INHIBITORS OF OZONE-INDUCED
DEGRADATION OF GR-S.
Anal. Chem. 26:1589-1592. October 1954.

A simple, rapid, and reliable method was developed for screening large numbers of chemicals as antioxidants for GR-S and other elastomeric materials. This method utilizes the rate of change in viscosity of polymer solutions. It is based on the observation that ozone reacts with unsaturated polymeric material with resultant cleavage of the molecular chains. In dilute elastomer solutions this scission is reflected by corresponding decreases in solution viscosity.

The apparatus comprises a transformer, an ozone generator, a rotameter flowmeter, an ozone reaction chamber, and an oxygen supply. A stream of ozonized oxygen containing 50 ppm ozone flowing at the rate of 0.05 cu m per hr is bubbled through 600 ml of polymer solution at room temperature. Aliquot portions of the ozonized solution are removed at intervals for viscosity measurements, using a Cannon-Fenske-Ostwald type viscometer. The polymer solution is prepared by dissolving 0.50 g purified GR-S (X-478) in 100 ml redistilled o-dichlorobenzene. Then 1-12 parts of the test antioxidant per 100 parts rubber is dissolved in the diluted solution.

On the basis of viscosity change in solutions containing 8 parts chemical per 100 parts rubber the following observations were made: Of six chemicals tested N,N-di-sec-butyl-p-phenylenediamine was the best inhibitor. In descending order of protective capacity were nickel dibutyl dithiocarbamate, 6-ethoxy-1,2-dihydro-2,2,4-trimethyl-quinoline, and 1-(m-aminophenyl)-2,5-dimethylpyrrole. A 65% phenyl-1-naphthylamine-35% diphenyl-p-phenylenediamine mixture and 2,6-di-tert-butyl-4-methylphenol accelerated the rate of ozone degradation.

In the range of 0-8 parts N,N'-di-sec-butyl-p-phenylenediamine per 100 parts rubber, an increase in concentration produced a corresponding decrease in the rate of polymer degradation. An increase to 12 parts produced no further change. Replenishment, after a 2 hr run, of a solution originally containing 8 parts of this antioxidant retarded the viscosity decrease, indicating that the

antiozidant is destroyed by ozone. No significant inhibiting effect was noted with 8 parts inert quartz powder particles per 100 of rubber. Under the experimental conditions of the test oxygen alone had no apparent effect on the viscosity index of the polymer solution.

The validity of the viscometric method for unvulcanized rubber was checked by ozonizing vulcanizates containing the antiozidants and determining the extent of surface cracking by the surface-replica techniques and by crack-depth measurements.

G-10777

Reich, M.H., T.B. Harrison, and B.G. Labbe.
STORAGE STABILITY OF GR-S POLYMERS.
Rubber World 130:789-794,800. September 1954.

Mooney viscosity, chemical test, and stress-strain determinations conducted on various lots of GR-S-1000, GR-S-1003, and GR-S-1004 (GR-S-AC) polymers revealed that little change in polymer properties occurred during storage periods as long as 5 yr. Polybutadiene and copolymers of butadiene and styrene, α -methylstyrene, chlorostyrene, dichlorostyrene, and vinylpyridine showed little change in viscosity. Differences of ± 15 ML-4 Mooney viscosity units occurred with butadiene-isoprene copolymers and a butadiene-styrene-divinylbenzene tripolymer in about 5 yr. A tripolymer of butadiene/styrene/divinylbenzene had poor aging properties, increasing in viscosity by 48 ML-4 units during 39-mo storage.

Accelerated aging by treatment of the raw polymers for 48 hr at 212 F in air caused relatively large changes in Mooney viscosity for GR-I-18, GR-S-1000 (X-603) and GR-S-1500 (X-632). The viscosities of another GR-S-1500 polymer (X-624) and a polybutadiene (XP-155) remained constant. Even with these large changes in Mooney viscosity, however, the stress-strain properties for vulcanizates of the preheated GR-I-18 and X-603 did not differ radically from those for the non-preheated vulcanizates. The X-632 vulcanizates of the preheated stock underwent the largest change, a loss of about 50% of their original tensile strength during accelerated aging.

G-10844

National Research Council. Advisory Board on Quartermaster Research and Development.
PROCEEDINGS JOINT ARMY, NAVY, AIR FORCE CONFERENCE ON ELASTOMER RESEARCH AND DEVELOPMENT, THE PENTAGON, JANUARY 12 AND 13, 1954.
National Research Council. Publication 370. September 1954.

The purpose of this conference was to present and discuss the military rubber problems, the progress made toward solution of these problems, anticipated requirements, and future plans.

Progress on the following topics was reported during the first session: Review of end-items progress; New rubber problems of the Department of the Army; Status of the Army rubber-research program; The elastomer program of the Bureau of Ships; The elastomer program of the Bureau of Aeronautics; Office of Naval Research report; The future military elastomer research program; Current Air Force rubber problems; Status of the Air Force rubber-research program; Office of Synthetic Rubber Research related to defense requirements: Polymerizations by the Nitrazole-CF formula, low-styrene GR-S plasticizer

masterbatches, and latex for the Army Prosthetics Research Laboratory; University of Illinois synthetic rubber research related to defense requirements; The industry-sponsored rubber research program.

The second session comprised elastomer deterioration research, replacement of natural rubber, and other areas of elastomer research. Individual report titles are as follows: Deterioration of elastomers; Aging studies on commercial vulcanizates; The continuous measurement of atmospheric ozone by an automatic photo-electric method; Methods for the evaluation of chemical protectants as inhibitors of ozone-induced degradation of GR-S; Replication methods for the investigation of ozone surface effects on elastomer compounds; Radioisotope-tracer techniques for the quantitative measurement of surface-cracking in elastomers; Determination of loss of plasticizers in vulcanizates by volatilization; Development of high-synthetic-content truck tires; Development of a tire tester; The synthesis of oriented high polymers; Biosynthesis of rubber; Synthesis of rubber by microorganisms; Fluorine-containing elastomers; Compounding and processing of poly 1,1-dihydroperfluorobutyl acrylate (Poly-FBA); Flow properties of liquid polysulfide compounds and effect upon flight-deck calking; and Problems in development of oil-resistant arctic rubber.

G-11555

Youmans, R.A. and G.C. Maassen.
CORRELATION OF ROOM TEMPERATURE SHELF AGING WITH ACCELERATED AGING.
Ind. Eng. Chem. 47:1487-1490. July 1955.

Vulcanized samples of a 50/50 smoked sheet—pale crepe rubber compounded with 40 parts carbon black, with and without antioxidant, were stored unwrapped up to 22 yr in a desk drawer. Physical properties were measured periodically, and attempts were made to duplicate the changes in three accelerated aging tests—air oven at 70 C, oxygen bomb at 70 C, and air bomb at 127 C.

Over 22-yr storage, antioxidant content decreased from 2 to 1% (based on rubber hydrocarbon). Owing to volatilization and migration, unprotected samples acquired 0.2% antioxidant content during the same period. Not all physical properties changed at the same rate during natural storage. During accelerated aging, not all properties changed at the same relative rates as during natural aging. None of the three accelerated tests predicted accurately all the physical changes occurring on long-time storage. All three heat-aging tests predicted with some degree of accuracy the trends in breaking tensile and breaking elongation during limited long-term storage. The air-bomb test was the least, the circulating-air oven the most reliable for predicting modulus changes at normal temperatures. The air-oven test predicted shelf life up to 6 yr for the vulcanized stock investigated.

G-11556

Milnes, Dale J.
ARTIFICIAL WEATHERING OF RUBBER. THE OZONE FACTOR IN WEATHERING
AND A TECHNIQUE FOR GENERATION AND CONTROL OF AN OZONIZED
ATMOSPHERE.
Rubber Age (N.Y.) 76:875-878. March 1955.

The Mast Ozone Test Chamber was devised to study the mechanism and prevention of rubber weathering. The apparatus consists of an ozone production and control unit and an ozone chamber in which is mounted a flexing and stretching apparatus. Ozone is generated by ultraviolet lamps whose operation is controlled by the conductivity of a potassium iodide solution. The conductivity of this solution is determined by the rate of injection and normality of the iodine-neutralizing sodium thiosulfate. This control system maintains selected ozone concentrations within a probably error of 2% at 2000 pphm. The range of ozone concentration can be varied from 1-10,000 pphm of air.

The flexing and stretching device (Dynamat) is included because cracking is never observed unless rubber is under stress, and ozone reaction rates on natural and synthetic rubbers are a function of elongation. The Dynamat is two-tiered to permit simultaneous static stress in the lower tier and dynamic exercise in the upper tier during the same cycle. It will hold eight samples with extent of flex (throw) adjustable up to 1 1/4 in. at frequencies from 50 to 250 cycles per min. Temperature can be varied from ambient to 200 F. The entire Dynamat is continuously rotated at 1-6 rpm.

G-11562

Ossefort, Z.T. and W.J. Touhey.
OZONE CRAZING OF BIAXIALLY STRESSED GR-S VULCANIZATES.
Rubber World 132:62-63,70. April 1955.

Cross-shaped specimens, 3 by 3 by 0.080 in., of vulcanized GR-S 1505 tire-tread stock were subjected to various degrees of biaxial stress and exposed to 25 pphm ozone in a dark cabinet at 100 F. One control sample was also exposed outdoors. Periodic examination at 20 X magnification indicated that crazing of stressed GR-S vulcanizates, which was previously attributed solely to oxidation activated by light, can be caused also by ozone in the absence of light. The experimentally produced crazing was identical with that produced in tire sidewalls during service.

G-11749

Buist, J.M.
AGING AND WEATHERING OF RUBBER.
Rubber Chem. and Technol. 28:230-252. January - March 1955.

G-11883

DeBaene, E.C. and C.A. Anderson.
MOISTURE STUDIES ON OZONE RESISTING AND TYPE RH-RW RUBBER INSULATIONS.
Power Apparatus and Systems No. 16:1746-1754. February 1955.

Eight brands of 'ozone-resisting' and ten brands of Type RH-RW rubber compounds were evaluated for possible use as 600-v nonleaded wire and cable insulation in wet locations up to 60 C. Except for

one natural rubber ozone-resisting formulation, all brands were based on Buna S rubber. Three samples of each brand were tested for power factor and breakdown voltage during and after water immersion for 25-32 mo at 50 C. One sample was energized with 300 v negative d-c potential with respect to the water tank, one sample was energized with 300 v positive potential, and one sample was left unenergized. In addition, accelerated oxidation behavior was judged by changes in physical properties.

The times-to-failure differed widely between different brands of both the ozone-resisting and the RH-RW type insulations. This indicates that good moisture-resistant properties depend largely on the proper selection and compounding of ingredients by the manufacturer and upon good processing techniques. As a class, however, the Type RH-RW compounds showed longer test life than the ozone-resisting compounds. After 25-mo immersion, all eight brands of the latter class had failed, whereas six of the ten RH-RW brands were still serviceable. In general, none of the test formulations was significantly affected by d-c potential. The negatively energized sample of each brand usually failed first, followed by the positively energized and, lastly, by the unenergized sample.

Long-time immersion tests, although impractical for specification purposes, seem essential in appraising the suitability of rubber compounds for service in wet locations. The provisions for moisture-resistance testing in present industrial specifications are of doubtful reliability for assessing the merits of rubber insulations.

G-11925

Case Institute of Technology, Cleveland, Ohio. Dept. of Chemistry and Chemical Engineering.
RESEARCH ON OXIDATION AND AGING OF NATURAL AND SYNTHETIC RUBBER, submitted by J. Reid Shelton and William T. Wickham.
Report 4 (Final); U.S. Ordnance Corps. Contract DA33-019-ORD-1207. 1955.

G-11963

Case Institute of Technology, Cleveland, Ohio. Dept. of Chemistry and Chemical Engineering.
RESEARCH ON OXIDATION AND AGING OF NATURAL AND SYNTHETIC RUBBER, submitted by J. Reid Shelton, William L. Cox, and William T. Wickham.
Report 3; U.S. Ordnance Corps. Contract DA33-019-ORD-1207. 1954.

Results of a study of the initial stage of oxidation and aging carried out with two GR-S black stocks, one cured with sulfur and Santocure and the other with Tetrone A and Captax without elemental sulfur, showed that the sulfurless cure gave a stock which absorbed oxygen somewhat slower than the conventional stock.

A comparison of the oxygen-absorption curves obtained at 70, 50, and 30 C showed that the initial stage of more rapid reaction was prolonged at the lower temperature so that, in spite of the slower rate, the total amount of oxygen absorbed was greater before the curves leveled off and approached a constant rate. The difference between the two stocks was less at the higher temperature.

Stock cured without elemental sulfur suffered less change in physical properties than conventional stock, either when compared at

the same time of aging or after absorbing the same amount of oxygen. This was particularly evident for the modulus and elongation values at lower temperatures. The conventional stock showed a greater increase in modulus values for a given oxygen absorption at 50 C than at 30 C; the reverse was true for the stock cured without elemental sulfur.

Freshly prepared GR-S black vulcanizates stored in nitrogen, air, or oxygen for 21 days at 73 F showed no detectable differences on subsequent oxidation at 50 C. More crosslinking occurred during storage in nitrogen, resulting in reduced tensile strength and elongation and increasing the stress required to produce a given elongation. Little effect of these storage conditions was apparent in the properties after accelerated aging in oxygen at 50 C.

Oxidation potential is apparently not a useful criterion for selection of potential antioxidants because values for known antioxidants and antioxidants with no ozone protective action were similar. All antioxidants studied contained, or could be readily oxidized to, a structure containing an unsaturation of the type $=C=N-$ which would be expected to be reactive toward attack by a polar reagent such as ozone. If a reactive unsaturation is essential to provide the necessary reactivity toward ozone, oxidation potential would only be important where the compound first must be oxidized to provide such a structure before it can function as an antioxidant.

G-12059

Edwards, D.C. and E.B. Storey.
OZONE RESISTANCE OF BUTYL VULCANISATES.
Inst. Rubber Ind., Trans. 31:45-69. April 1955.

A study of the cracking behavior of Butyl rubber vulcanizates exposed under static strain to an atmosphere containing 25 ppm ozone at 120 F reveals that cracking increases moderately with increasing raw polymer unsaturation and decreases markedly with increasing state of cure. Carbon black loadings in excess of 40 parts per 100 parts of polymer are desirable. Finer particle size blacks are superior to coarser blacks when compared at equivalent states of cure. FEF black give the best balance of processing, rate of vulcanization, and ozone resistance. Plasticizers are generally detrimental to ozone resistance, the effect being proportional to plasticizer loading but varying considerably between plasticizers. The eight antioxidants tested are all of some benefit, but none offer complete protection at conventional loadings. Waxes and antioxidants together are more beneficial, but Butyl rubber requires higher proportions of wax to ensure a continuous bloom than do other elastomers. Variations in laboratory mixing and processing techniques cause no substantial changes in the tendency to crack.

By a careful selection of plasticizers, and with a suitable state of cure, low-cost, highly ozone resistant compounds can be obtained without reliance on waxes or excessive loadings of antioxidants.

A new method for rating the severity of cracking in triangular strip specimens involves both visual examination and measurement of number and depths of cracks.

G-12192 DETAILS OF AKRON RUBBER GROUP'S PROTECTIVE MATERIALS SYMPOSIUM.
 II. QUESTIONS AND ANSWERS.
 Rubber World 132:623-625. August 1955.

G-12251 Sharpe, Paul D.
 PETROLEUM WAXES FOR PROTECTING RUBBER COMPOUNDS FROM CRACKING:
 THE RELATIVE MERITS OF OZONE-EXPOSURE TESTING AND NATURAL
 AGING OF RUBBER.
 Rubber Age (N.Y.) 77:884-890. September 1955.

Little correlation exists between the results of accelerated aging and outdoor exposure tests of the ozone cracking of GR-S rubber containing various waxes as protective agents.

Two straight high-melt paraffin waxes were rated as excellent on outdoor aging but poor or very poor on accelerated aging. One proprietary blended wax gave very poor outdoor but excellent ozone exposure results while two others were medium-to-poor and poor on outdoor aging but gave good ozone exposure results. Twelve of the twenty specimens, including the control, had outdoor ratings within one unit of their accelerated test ratings although the extent of cracking in ozone chamber samples was considerably greater in all cases than was that of the outdoor samples.

Natural aging specimens were looped and mounted on lacquered boards, held for 48 hr in the dark to develop a wax bloom, then exposed outdoors under static conditions for 1 yr. Only three specimens showed no deterioration after 1 yr. These contained 3 PHR (parts per hundred of rubber) of paraffin wax. The performance of these waxes was attributed to the lack of dynamic flexing in the aged specimens. The flexion occurring in service causes flaking of the paraffinic waxes which are rapid blooming and have large crystals. A special blend of microcrystalline and paraffinic waxes added in amounts of 4-5 PHR gave significantly increased protection.

Accelerated ozone testing was carried out in a modified Crabtree-Kemp ozone chamber with an ozone concentration of 1-3 ppm of air following the procedures of ASTM D-1149-51-T and D-470-52-T. Three sets of samples were tested by exposure for 1 hr in the ozone chamber at 75 F. These included specimens which were placed in the chamber immediately after 20% elongation; those held for 48 hr at 20% elongation in ordinary atmosphere prior to ozone exposure; and those which were held at 20% strain for 24 hr at 120 F before exposure. Deterioration was generally most severe in those specimens exposed immediately after stretching so that the wax film had no chance to reform on the elongated surface. Specimens held at 120 F for 24 hr showed the least deterioration. This interval was felt to be sufficient to equalize variations in resistance due to different wax blooming rates so that differences in results could be attributed to the inhibitors alone. Under these test conditions excellent protection was given by a proprietary blended wax used in a concentration of 3 PHR, a blended wax containing 5% polyethylene, and a blended wax at 4 PHR. The addition of 10% polyethylene to the wax destroyed the improvement noted with the 5% addition.

- G-12375 Augustana Research Foundation, Rock Island, Ill.
STUDY OF REACTION OF OZONE WITH POLYBUTADIENE RUBBERS.
Report No. 7; U.S. Ordnance Corps. Contract No. DA-11-022-ORD-329.
February 1955.
- G-12430 Braden, M. and W.P. Fletcher.
THE PROTECTION OF NATURAL RUBBER AGAINST ATTACK BY OZONE.
Rubber J. 129:709-710. November 1955.
- G-12439 Winkelmann, Herbert A.
WEATHERSEALS IN AUTOMOTIVE APPLICATIONS.
Society of Automotive Engineers, New York, N.Y. Preprint 468. 1955.
- Over 3000 automotive weatherseal specimens of dense and sponge rubber were exposed on 2-in. mandrels with the axis running east and west on a lake shore in Maine and in Chicago. The tendency of the samples to crack was 2 to 2 1/2 times greater on the northern than the southern exposure. This difference showed up at all seasons of the year. Mandrel test results were confirmed on tires on new cars facing alternately north and south on a storage lot.
- Molded and extruded weatherstrips exposed with and without a 1/4 in. chrome plated band placed around the center of the test specimen showed decreased cracking in the presence of the chrome strip.
- To study the effect of seasonal variations on cracking, identical specimens from controlled batches were exposed in Florida, Massachusetts, California, Michigan, and Chicago during two summers and from September through March. The degree of cracking varied from year to year, from season to season, and from site to site. Chicago and Michigan exposures gave the most cracking; Florida and California showed the least. In all locations except Michigan there was more cracking during the summer than during the winter.
- Tests made in ozone chambers in two different laboratories checked reasonably well with each other and fairly well with 30-day outdoor exposure results from Chicago. Exposures of 1 and 2 yr in Chicago, however, caused more cracking than was indicated by the ozone chamber tests using 25 parts ozone per 100 million of air at 100 F for 70 hr.
- G-12537 Gaughan, James E.
OZONE CRACKING OF NATURAL AND SYNTHETIC RUBBERS.
Rubber World 133:803-808. March 1956.
- G-12585 California Institute of Technology, Pasadena. Division of Biology.
OZONE RESISTANT COMPONENTS, by John W. Brooks.
U.S. Ordnance Corps. Contract DA-04-200-ORD-475, Report 27.
March - April 1956.

G-12586 California Institute of Technology, Pasadena. Division of Biology.
OZONE RESISTANT COMPONENTS, by John W. Brooks.
U.S. Ordnance Corps. Contract DA-04-200-ORD-475, Report 28.
April 1956.

G-12763 Kendall, F.H. and J. Mann.
REACTION OF OZONE WITH NATURAL HEVEA AND ACRYLONITRILE-BUTADIENE
RUBBERS.
J. Polymer Sci. 19:503-518. March 1956.

Studies carried out on thin films of Hevea rubber and monolayers of Hycar OR-15 show that during ozonization spontaneous scission occurs at the carbon-carbon double bond with the production of aldehyde and/or ketone and a peroxy biradical. A chain reaction presumably takes place which is inhibited by 1% phenyl-2-naphthylamine. Its suppression does not, however, prevent the cracking of stretched vulcanizates.

Changes in physical characteristics were studied on pure gum vulcanizates at temperatures varying from 30 to 100 C. Surface clouding, loss of rubbery properties, and translucence accompanied the formation of a white film on the specimens. Time required for cloud formation varied from less than 15 sec at 100 C to 900 sec at 30 C. At 40 C, clouding took place in 60 sec, whereas 450 sec were required at 35 C. Moisture appears to be unnecessary for this reaction because surface clouding took place even with carefully dried rubber and ozone. Ozonized oxygen, however, produced no clouding.

The attack of ozonized air or oxygen on unstretched, unvulcanized natural rubber was demonstrated with films about 200 A thick. Within a few seconds these films lost cohesion on exposure to air containing 0.01% ozone; films 1 μ thick retained their rubbery properties for hours. The speed of reaction thus appears controlled by diffusion of gas into the rubber; as a consequence, initial products formed near the surface are subjected to further action by ozone.

Of eight antioxidants other than phenyl-2-naphthylamine in natural rubber vulcanizates, none provided protection against ozone cracking. Some appeared to influence slightly the rate and volume of cracking. 10-25% ester-type wax, 5-15% phospholipides, and 25-35% vegetable oil. A preferred antioxidant is obtained by extracting dehydrated alfalfa with a mixture of naphtha and any low-boiling alcohol or ketone. At the concentrations indicated, the antioxidants do not impart a green color or alfalfa odor to the wax. Thus, a paraffin wax containing 0.67 ppm of an antioxidant prepared as above did not oxidize when held at 200 F for 26 days.

G-12803 Buckley, D.J. and S.B. Robison.
OZONE ATTACK ON RUBBER VULCANIZATES.
J. Polymer Sci. 19:145-158. January 1956.

Cracking of the surface of vulcanizates exposed to ozone under strain was studied quantitatively. The use of Butyl rubber vulcanizates permitted ready variation of polymer unsaturation. When it is exposed to ozone, a relaxed sample under tension undergoes a work

change manifested by increased length and decreased stress as cracking occurs. The change in work is considered related to the generation of new surface in the form of cracks. Cracking is found to be primarily a surface phenomenon, hence permeation of the ozone into the sample assumes an important role in this phenomenon since it defines the 'depth of the surface'. Polymer structure as it affects permeation appears as important as chemical inertness in controlling ozone cracking. The amount of cracking judged by change of work measured in these experiments is related linearly to the time squared. The rate of cracking is related linearly to ozone concentration squared over the range 0.03-0.20 volume percent in air. The rate and type of cracking are dependent on extension. The analysis of this relation is complicated by relaxation effects. The state of relaxation of a sample under tension has a profound effect on the rate of ozone cracking. This effect is discussed in terms of distribution of strain of the network chains. Although cracking requires a stored energy to produce new surface, the chemical action of ozone proceeds in the absence of strain. Whether the effects of polymer degradation under conditions of zero strain become large enough to be measured depends on the rate of permeation of ozonized air into the specimen.

Vulcanization has an important bearing on ozone cracking in Butyl rubber. This probably is due to a significant decrease in the percentage of unreacted double bonds and also to a local densification of the network in the region of the double bond involved in a crosslink. Cracking is particularly sensitive to the onset of reversion. This sensitivity may arise because the state of reversion may be a gradient, greatest on the surface and least at the center of the sample.

In this study, square shoulder T-50 specimens of Butyl-rubber, 0.25 cm wide and 5 or 12.5 cm in length, were used. The head and square shoulders, points of excessive strain, were coated with silicone grease to minimize cracking. The sample was stretched and allowed to relax until most of the pertinent stress relaxation had taken place before ozone was admitted. Relaxation and ozonization were carried out at 25 C.

G-13126

Merrifield, D. Bruce.

HIGHLY STABILIZED NON-DISCOLORING RUBBER COMPOSITIONS.

Rubber World 134:415-421. June 1956.

A natural rubber white sidewall base formulation is nonstaining, nondiscoloring, and highly resistant to ozone and heat aging; it also has excellent processing characteristics. Tests were run on both a 4,4'-dithiodimorpholine-vulcanized and a sulfur-vulcanized system. Dithioamine systems have unusual scorch delay, but once started their rate of vulcanization is more rapid than that of conventional systems.

Four antioxidants were used in these studies: two sterically hindered bis phenols, a thiobis phenol (4,4'-thiobis(6-tert-butyl-m-cresol)), and a hindered hydroquinone (2,5-di-tert-amylhydroquinone). None of these provided ozone resistance in a conventional formulation, but all were active in dithioamine stock. The hindered hydroquinone provided the greatest ozone resistance although it was the least active in sulfur vulcanizates.

The dithioamine stock without antioxidant retained 64% of its original tensile strength after air-oven aging for 96 hr at 100 C. This was increased to 84 to 88% when antioxidant was added. Traces (0.02 parts per hundred of rubber) of lead stearate added to dithioamine-vulcanized stock containing hydroquinone antioxidant enhanced the aging and ozone resistance of these stocks without discoloration caused by lead sulfide formation. Free radical mechanisms are postulated to explain some of the results.

G-13263

Edwards, D.C. and E.B. Storey.
EXPOSURE CRACKING OF SIDEWALL COMPOUNDS.
Rubber Age (N.Y.) 79:787-795. August 1956.

The cracking behavior of batches of Polysar S (hot GR-S) sidewall compounds containing (0.5 to 6 phr) wax and/or (0.5 to 2 phr) antiozinants was studied. Both wax and antiozinant decreased the number of cracks at a given strain. The antiozinant also retarded the growth rate of the cracks. The protective action of wax-antiozinant mixtures was greater than would be expected from their individual performances, and the use of such combinations provided the best protection. Mechanical failure of the surface wax film was not observed in the sidewall test, even with as high a loading as 6 parts of wax.

Three types of experimental procedure were used: (1) Static exposure of spirally deformed specimens in a controlled ozonized atmosphere showed the effects of strain on cracking. (2) A microscopic study of strip specimens exposed at 20% strain provided information on the induction period, number, and growth behavior of cracks. (3) The exposure of specimens mounted on the sidewall of a tire was a simple and economical means of testing under conditions nearly identical to those of actual service. The first two tests were carried out in an atmosphere containing 25 parts ozone per hundred million parts air at a temperature of 120 F. In the sidewall test, strip specimens 0.030 in. thick were cemented and vulcanized to the sidewall and the tire mounted on a test car driven for 56 days. Every 7 days the tire was removed, washed with water, and inspected. After service the specimens were removed from the tire and elongated 20% for photographing.

G-13390

Zuev, Y.S.
THE PROTECTION OF RUBBERS AGAINST OZONE CRACKING.
Rubber Chem. and Technol. 28:788-792. [1955].

G-13455

Bresee, J.C. and others.
DAMAGING EFFECTS OF RADIATION ON CHEMICAL MATERIALS.
Nucleonics 14(9):75-81. September 1956.

P-63

Rittschof, William L. and Wayne A. Proell.
METHOD OF PROTECTING RUBBER PRODUCTS.
U.S. Pat. 2,392,881; January 15, 1946. 2 p.

This invention claims a method of preventing the crazing or other deterioration of synthetic rubber which comes in contact with liquid aromatic hydrocarbons, motor fuels, hydrocarbons in the presence of copper, or motor fuels containing a substantial amount of liquid aromatic hydrocarbons, which normally cause the deterioration of the synthetic rubber. Protection is claimed to be provided by the use of 0.0005% to about 1% of an aliphatic polyamine containing at least 4 amine groups of which two are primary amino groups. The polyamine may be an alkylene polyamine, triethylene tetramine.

Data are given showing actual tests which have been performed to measure the protective action of these compounds.

P-333

Howland, Louis H. and Byron A. Hunter.
PRESERVATION OF SYNTHETIC RUBBER.
U.S. Pat. 2,419,354; April 22, 1947. [2] p.

This preservative inhibits deterioration induced before vulcanization, by oxygen, heat, or light in synthetic elastomeric materials which are derived from 1,3-diene polymers. The preservatives may be used in either white or colored synthetic rubber stocks, as no discoloration occurs from exposure of the treated samples to sunlight.

The preservative consists of an organic ester of phosphorous acid containing three identical aryl radicals. Examples are triphenyl phosphite and tri-*o*-tolyl phosphite, among many others. The phosphites are conveniently prepared by reacting 1 mol of phosphorus trichloride with 3 mol of the appropriate phenol until the evolution of hydrogen chloride is complete.

Treated and untreated samples of butadiene-styrene copolymer were heated in an oven at 212 F for 24 hr and then examined. Treated samples, containing 2 parts phosphite per 100 parts copolymer, were all in good condition, showing no deterioration. The surface of the untreated stock was resinified and cracked easily on bending. On replacing the samples in the oven and examining them daily for 10 days, the untreated rubber was found to be increasingly harder although the treated retained the appearance of the original unaged copolymer.

The amount of deterioration inhibitor used may vary, economical proportions being 0.25 - 5.0 parts by weight per 100 parts of elastomer. The inhibitor may be used alone or with other preservatives, fillers, accelerators, vulcanizing agents, or compounding agents; and in such rubber articles as tubes, hose, vehicle tires, and boots. It may be incorporated into the elastomer by milling, by mixing with the synthetic rubber latex before or during coagulation, or by application on the surface of the crude polymer or vulcanized product.

P-459 Imperial Chemical Industries Limited, London.
IMPROVEMENTS IN THE PRESERVATION OF RUBBER AND THE LIKE.
Gt. Brit. Pat. Spec. 581,099; October 1, 1946. [8] l.

P-682 Downing, Frederick B. and Charles J. Pedersen.
PRESERVATION OF RUBBER.
U.S. Pat. 2,442,200; May 25, 1948. [5] p.

The decomposition of rubber by molecular oxygen may be prevented even in the presence of such oxidation catalysts as copper, cobalt, iron, or their compounds by adding a small portion of a metal deactivator having the formula



where R and R' are bivalent aromatic radicals. The preferred aromatic radicals contain only one benzene ring and no nonhydrocarbon substituent groups. The OH group in each case must be ortho to the CH=N group.

Particularly effective compounds are salicylidene-o-aminophenol and 2-hydroxy-3-methoxybenzylidene-o-aminophenol. From three to ten times as much of the deactivator should be used as the amount of the metal in the rubber; greater amounts may be necessary if the metal is present in bulk form.

P-896 Howland, Louis H.
PRESERVING SYNTHETIC RUBBER.
U.S. Pat. 2,460,177; January 25, 1949. [2] p.

P-949 Goodrich (B.F.) Company, Akron, Ohio (Arthur William Sloan).
IMPROVEMENTS IN OR RELATING TO THE PRESERVATION OF RUBBER OR RUBBER-LIKE MATERIALS.
Gt. Brit. Pat. Spec. 580,740; September 18, 1946. 6 l.

P-1103 Hart, Edwin J.
PRESERVING RUBBER.
U.S. Pat. 2,476,661; July 19, 1949. [2] p.

Rubber and similar vulcanizable materials are made much less susceptible to oxidation and flex-cracking by the addition of 0.1 - 5% of a secondary aromatic amine antioxidant and a similar quantity of an organic tin compound having the formula $(\text{C}_6\text{H}_5\text{CH}_2)_3\text{Sn-R}$ in which R is an alkyl group having two to six carbon atoms.

Tribenzylethyltin is the preferred organic compound. The secondary aromatic amines may be any of the well known flex-cracking inhibitors, such as diphenylamine and N-phenyl-2-naphylamine, or mixtures of secondary aromatic amines resulting from the condensation of acetone or other ketones with simple diarylamines such as diphenylamine.

P-1463

Blake, Edward S.
PRESERVING RUBBER.
U.S. Pat. 2,506,410; May 2, 1950. [4] p.

Effective antioxidants for rubber are provided by polyhydric phenols having at least 1 nuclear hydrogen replaced with an aryl-substituted ethyl group. The aryl group should be separated by no more than 2 carbon atoms from the phenol nucleus. Examples of suitable compounds are diphenylresorcinol, phenethylcatechol, and diphenethylhydroquinone. One part antioxidant is used per 100 parts rubber. The compounds produce no discoloration in white rubber stocks.

The antioxidants can be prepared cheaply and easily by reacting, in the presence of an acid catalyst, approximately 2 mols of a vinyl aromatic compound such as styrene, with 1 mol of a dihydric phenol. A reaction temperature below 100 C is generally desirable.

P-1570

McMillan, Frank M.
CRACK-RESISTANT VULCANIZED RUBBER AND METHOD FOR ITS PRODUCTION.
U.S. Pat. 2,514,661; July 11, 1950. [6] p.

Vulcanized rubber, either natural or synthetic, can be rendered resistant to ozone attack and atmospheric cracking by incorporating, prior to vulcanization, 0.02-10% by weight of a stabilizer formed by reacting an unsaturated organic compound with hydrogen sulfide or a mercaptan. Suitable unsaturated organic compounds are olefins, unsaturated ethers, and thioethers; diallyl ether and dimethallyl ether are preferred.

From 0.5 to 2 mols unsaturated compound, 1 mol hydrogen sulfide or mercaptan, and 1-10 mol per cent, preferably 2-5, catalyst such as aluminum chloride or piperidine, are combined at 25-150 C; a pressure of 50-1000 psi accelerates the reaction. Fractions of the reaction product volatilizing below 100-150 C at 2 mm mercury pressure are preferably removed before the product is incorporated in the rubber mix.

P-1632

Jayne, David W., Jr. and Harold M. Day.
RUBBER-LIKE CURED POLYESTERS AND PROCESS FOR PREPARING SAME.
U.S. Pat. 2,489,711; November 29, 1949. [3] p.

Rubberlike cured polyesters are described that are superior to natural rubber in resistance to gasoline, grease, oil, light, heat, and air, but inferior in tensile strength and elongation. These polyesters are employed as molding, laminating, coating, and impregnating compounds, and can be blended with rubber as antioxidants, plasticizers, and accelerators. Textiles impregnated with a solution of the uncured polyester become water repellent when cured.

To prepare the polyesters, an ω -hydroxy saturated aliphatic carboxylic acid having 6-20 carbons, such as ω -hydroxycapric acid, is heated at 180-220 C, preferably 200 C, with a glycol acid ester of an α,β -unsaturated dicarboxylic acid such as glycol ester of maleic or fumaric acid, in a molar proportion ranging from 1:0.5 to 1:1. The resinous polyester is cured by heating with a small amount of an

organic peroxide catalyst. To increase tensile strength, the resin can be milled with a pigment such as iron oxide, together with 1-10% (by weight of resin) of an organic peroxide catalyst such as lauroyl peroxide and cured under heat and pressure.

Other suitable acids include ω -hydroxystearic acid and ω -hydroxymyristic acid. Curing catalysts include acid peroxides, fatty oil acid peroxides, alkyl peroxides, and terpene peroxides.

P-1736

Hansen, Louis I. and George E.P. Smith, Jr.

STABILIZATION.

U.S. Pat. 2,514,198; July 4, 1950. [9] p.

Stannous salts of catechol and alkyl derivatives of catechol which contain 1-10 carbons are effective non-discoloring stabilizing agents for rubberlike copolymers of a conjugated diene and a vinyl or methyl-substituted vinyl compound. The stabilizer is preferably added in a sodium oleate emulsion to the latex although it may be added at any stage of copolymer preparation.

Addition of 2% stannous catecholate to the latex resulting from copolymerization of 1,3-butadiene and styrene produced better percentage retention of tensile strength and elongation on aging than when a similar quantity of a commercial stabilizer was used. The catecholate did not discolor the copolymer during vulcanizing, or during aging for 10 hr in a fadeometer at 125 F or under a sun lamp for 16 hr. The stabilizer compared favorably with a commercial stabilizer when added in 2% quantity to latex compounded from 1,3-butadiene and acrylonitrile or methacrylonitrile.

P-1739

Cline, Delbert C.

NEOPRENE-POLYBUTADIENE FREEZE-RESISTANT COMPOSITION.

U.S. Pat. 2,514,194; July 4, 1950. [3] p.

The subzero freeze resistance of neoprene is improved by the use of polybutadiene as a softener. In addition, the rubbery composition has superior tensile strength, elongation, and flexibility when compared with other elastomers of similar freeze resistance, such as Buna S, Buna N, or their blends.

The composition contains 60-90 parts neoprene and 10-40 parts polybutadiene made by polymerization to 80% conversion in aqueous emulsion at 122 F.

Polybutadiene can be advantageously substituted in any neoprene composition for any plasticizer used to increase freeze resistance, such as Circo light oil, dibutyl sebecate, or dibutyl phthalate. Four times more Circo light oil than polybutadiene per unit weight of neoprene was needed to obtain an 8 F increase in freeze resistance. This increase for Circo light oil was accompanied by a decrease in tensile strength of 1700 psi, as compared with a loss of only 300 psi for the polybutadiene composition.

Various samples of freeze-resistant neoprene were flexible to within 3 F of their brittle points. Since less polybutadiene than other softeners is necessary to increase freeze resistance, neoprene is not substantially diluted, and the inherent advantages of neoprene such as resistance to oil, flame, and heat are not nullified.

P-1852

Spicer, Alvin W.
SUNLIGHT PROTECTION FOR DISTORTABLE RUBBER SURFACES.
U.S. Pat. 2,531,541; November 28, 1950. [4] p.

A vinyl resin coating containing flakes of aluminum, mica, or graphite has been developed to protect distortable rubber surfaces, especially inflatable rubber shoes for ice-removal on aircraft. The coating is applied to shoes in the summer and peeled off for winter operation; this eliminates the necessity for removing the shoes during the summer.

The coating reflects light effectively and is extremely resistant to deterioration by sunlight, weather, ozone, and oil. It is characterized by its stretchability, toughness, and ability to adhere well to the rubber and yet remain intact in the peeling operation. The flakes overlap in a shingled effect, providing electrical protection and mobility during stretching.

Two or three parts by weight of aluminum flakes, 10-200 μ in size, are added to an aqueous dispersion of a plasticized water-insoluble vinyl resin containing 42% resin solids and having a viscosity of 30. The flakes can be a mixture of mica having a specific gravity of 3 and a size of 5-200 μ , and graphite having a size of 1-100 μ . The dispersion is applied to a clean surface, preferably by spraying. Three coats, resulting in a layer 0.007 in. thick, give good protection. A 0.020-in. layer does not interfere with the distention or inflation of the shoe.

The resin composition can be polyvinyl butyral, polyvinyl acetal, polyvinyl chloride, a mixture of polyvinyl chloride and polyethyl acrylate, or mixtures of these. Satisfactory plasticizers include tricresyl phosphate, dibutyl phthalate, or dioctyl phthalate. A dispersing agent such as a suitable soap and a stabilizer such as ammonium hydroxide can be included.

P-1885

Newby, Thomas H.
VULCANIZED RUBBER AND METHOD OF PRESERVING SAME.
U.S. Pat. 2,549,118; April 17, 1951. [3] p.

Aliphatic thioethers of hydroquinone protect natural and synthetic rubber against exposure to heat, light, and oxygen. From 0.05 to 5.0 parts antioxidant is added to 100 parts rubber before vulcanization.

The antioxidant is a 1,4-dihydroxybenzene substituted on the benzene ring with one or more -SR groups, R being an aliphatic radical; the only groups bonded to the sulfur are the benzene ring and R. These compounds can be prepared by reacting p-benzoquinone with an aliphatic compound containing a single thiol group such as dodecanethiol and butanethiol. The reaction is carried out in a polar solvent at a temperature between 0 C and the boiling point of the solvent, and the resulting product is treated with sodium hydro-sulfite.

Tensile strength tests were made on an unaged natural rubber white stock, cured 20 min, containing 1.0 part 1,4-dihydroxyphenyl dodecyl sulfide per 100 parts rubber. The rubber had a tensile strength of 1930 psi; after aging 96 hr under 300 lb oxygen at 70 C the tensile strength was 1050 psi. A similar sample without the antioxidant failed.

P-1988

McMillan, Frank M. and David E. Adelson.
CRACK-RESISTANT RUBBER AND METHOD FOR PRODUCING THE SAME.
U.S. Pat. 2,564,404; August 14, 1951. [7] p.

The resistance against atmospheric cracking of vulcanizates of natural rubber or of synthetic rubber derived from conjugated diolefins can be improved by adding 0.02-10% by weight of the rubber, of a ketone-sulfide additive. This additive is made by reacting phosphorus pentasulfide with a higher ketone containing at least 12 carbons in the molecule and having the ketonic carbonyl group as its only reactive group. Suitable higher ketones are obtained by topping the still bottoms from the caustic-catalyzed condensation of acetone to isophorone.

The improved crack resistance of these rubbery compositions over control materials containing no ketone-sulfide additive is not dependent on the formation of a protective film, and they are therefore effective under dynamic and static conditions.

P-1990

Karimullah, ?, Uma Shankar, and Gauri Shankar Tewari.
IMPROVEMENTS IN OR RELATING TO THE MANUFACTURE OF RUBBER COMPOUNDS FOR LINING OR SEALING CONTAINERS OR FOR MAKING DIPPED GOODS OR THE LIKE.
India. Pat. Spec. No. 36318; April 3, 1948. 7 l.

P-2287

Shokal, Edward C., De Loss E. Winkler, and Paul A. Devlin.
STABILIZATION OF HALOGEN-CONTAINING ORGANIC MATERIALS.
U.S. Pat. 2,585,506; February 12, 1952. [5] p.

Halogen-containing organic compounds, especially high molecular weight halogenated hydrocarbons and polyvinyl chloride, can be stabilized against heat and/or light by the addition of a polymeric epoxyalkyl alkenyl ether. This additive has at least three monomeric repeating units and at least three epoxide groups per polymer molecule, and an epoxide value of at least 20% of the theoretical maximum value. Volatile halogen compounds require 0.3-1% of the stabilizer; highly polymeric compounds require 2-5%. In addition, the epoxide can function as a plasticizer extender in polyvinyl chloride compositions. From 5 to 30% of the epoxide based on the weight of polyvinyl chloride is employed. This additive inhibits corrosion of metal containers and preserves good color.

Examples of epoxide stabilizers include poly(allyl glycidyl ether), allyl glycidyl ether-styrene copolymer, poly(vinyl glycidyl ether), and vinyl glycidyl ether-vinyl acetate copolymer.

A preferred method of preparing these stabilizers is by air-blowing a monomeric vinyl or allyl glycidyl ether at elevated temperature in the absence of alkaline or acid catalysts. As an example, allyl glycidyl ether was polymerized by refluxing at 155 C while a stream of air was introduced below the surface of the liquid. Air-blowing and refluxing were continued intermittently until the refractive index increased from n_D^{20} 1.4345 to 1.4764, with an epoxide value of 0.5 equivalent per 100 g, which is 57% of the theoretical value.

In addition to polyvinyl chloride, other nonvolatile compounds that can be stabilized by the epoxy polymers include polyvinylidene

chloride, polyfluorochloroethylene, copolymers of vinyl halides with other unsaturated compounds, and halogenated high molecular weight natural resins and hydrocarbons such as paraffin waxes and natural rubber. Volatile compounds that can be stabilized include 2-chloro-2-butene, trichloropropane, trichloropropene, 1,3-dibromopropane, 2-bromo-2-butene, allyl chloride, methallyl chloride, and isocrotyl chloride. Examples are given showing the stabilization of some of these typical compounds, as well as the use of the epoxy polymer as a plasticizer extender in polyvinyl chloride plastic.

P-2310

Kitchen, Leland J. and George E.P. Smith, jr.
BUTADIENE RUBBERY COPOLYMER STABILIZED WITH 2,4-DIMETHYL-6-OCTYLPHENOL.
U.S. Pat. 2,605,251; July 29, 1952. [3] p.

Cured and uncured butadiene copolymers can be stabilized against deteriorative changes on aging, such as stiffening, loss of tensile strength, discoloration or embrittlement, by the use of 2,4-dimethyl-6-octylphenols. The stabilizer is preferably added directly to the latex which results from the emulsion copolymerization. Since it is nondiscoloring, the stabilizer has special value in white or light-colored copolymer compounds. It also serves as antioxidant in the vulcanizate. The stabilized copolymer is capable of storage even at high temperatures without substantial deterioration. Ordinarily, less than 5 parts of stabilizer per 100 parts of copolymer are used.

P-2313

Hunter, Byron A.
RUBBER ANTICRACKING CHEMICALS.
U.S. Pat. 2,605,250; July 29, 1952. [2] p.

The monoöxalic acid salt of N,N'-di-sec-butyl-p-phenylenediamine is a new anticracking antioxidant for natural and synthetic rubber such as butadiene-styrene and butadiene-acrylonitrile copolymers. The addition of 0.1-5% of this salt to a rubber inhibits cracking under stress while weathering in air, heat, and/or sunlight. This salt is uniquely less toxic than N,N'-di-sec-butyl-p-phenylenediamine, which, although effective as an anticracking agent, is so toxic that it cannot be used commercially. The dioxalic acid salt has no value as an anticracking agent.

A cured GR-S rubber sheet containing 1.5% of the monoöxalic acid salt, bent double while weathering outdoors, developed slight cracks after 39 days and bad cracks after 67 days compared with 4 days and 7 days respectively, for the same rubber without the anticracking salt.

P-2337

Amberg, Lyle O.
PROCESS FOR THE PRESERVATION OF A RUBBER WITH A TERPENE MODIFIED PHENOL.
U.S. Pat. 2,606,886; August 12, 1952. [6] p.

Natural and synthetic rubber compositions containing 0.25-1.5%, based on the weight of the rubber, of a terpene-substituted phenol

are resistant to oxidation and discoloration and are nonstaining. These phenol antioxidants can be prepared by condensing cyclic terpenes having at least one ethylenic double bond with a phenol in the presence of certain catalysts such as boron trifluoride, anhydrous hydrogen fluoride, or activated siliceous materials. Terpenes having the empirical formula $C_{10}H_{16}$ as well as dihydro-terpenes, $C_{10}H_{18}$, are suitable. Any phenol can be employed.

P-2347

British Rubber Producers' Research Association, Welwyn Garden City, England (Claude Montague Blow and others)
IMPROVEMENTS IN AND RELATING TO THE TREATMENT AND USE OF RUBBER LATEX AND OTHER AQUEOUS DISPERSIONS.
Gt. Brit. Pat. Spec. 652,892; May 2, 1951. 5 l.

Corrosion of metallic surfaces by natural or synthetic rubber latices can be inhibited by adding to the latex up to 10% alkali metal, zinc, or magnesium benzoate, preferably sodium benzoate, and up to 2% sodium nitrite, based on the rubber content of the latex. The sodium nitrite should be about 20% by weight of the benzoate in the mixed inhibitor; preferably, the benzoate is 5% and the nitrite is 1% of the weight of the rubber. The benzoate alone inhibits corrosion, but not as effectively as the mixture, particularly in the case of cast iron. These treated latices do not corrode iron or steel storage containers. They can be used as strippable protective coatings on metallic surfaces.

Water-soluble salts such as sodium benzoate and sodium nitrite are added to the latex as saturated water solutions. Water-insoluble salts, such as zinc benzoate, are dispersed in water by grinding with a wetting agent, and then added to the latex. The chloride content of the latex should be as low as possible, preferably less than 0.1% based on the rubber content. The rubber in the latex can be unvulcanized, vulcanized, or vulcanizable, and the latex can be either in the normal or concentrated form.

P-2661

Slovin, David G.
PREVENTION OF PINKING IN RUBBER ARTICLES CONTAINING DI-BETA-NAPHTHYL-PARA-PHENYLENE DIAMINE ANTIOXIDANT.
U.S. Pat. 2,610,983; September 16, 1952. [3] p.

The tendency for vulcanized rubber containing 0.25-2.0% of the antioxidant di-2-naphthyl-p-phenylenediamine to turn pink when it is subjected to light, bleaches, and certain oxidizing media such as nitric oxide fumes and ozone, is prevented by adding to the rubber compound prior to vulcanization 0.25-5.0% of 2,5-di-tert-butylhydroquinone. This nonpink rubber is especially suited to the manufacture of elastic yarn made with a core of tensioned elastic vulcanized rubber and wound with white or light-colored yarn.

N,N'-bis(p-dimethylaminophenyl)thiourea, N-phenyl-N'-(p-hydroxyphenyl)thiourea, and N-phenyl-N'-(p-dimethylaminophenyl)urea.

A typical compounded rubber stock containing 1% N,N'-bis(p-dimethylaminophenyl)thiourea retained 43.3% of its original tensile strength and 71.5% elongation after aging, compared with 24.5% tensile strength and 55% elongation for the same stock without stabilizer.

P-3028

Harvey, Mortimer T.
METHOD OF INCREASING OZONE RESISTANCE OF RUBBERY POLYMER AND
PRODUCTS OBTAINED THEREBY.
U.S. Pat. 2,678,892; May 18, 1954. [2] p.

The resistance to aging, ozone, corona, and sunlight of articles or coatings of vulcanized natural, GR-S, chloroprene, and Buna-N type rubbers, such as fuel hose, electric insulating tubes, and tires, can be improved considerably by treating them with hydrogen at 110-140 C and at least 40 psi pressure for 48 hr or for shorter periods at correspondingly higher temperatures and pressures. Preferably, the length of treatment should be adequate to secure a hydrogen take-up of at least 2 cu cm per sq in. of surface. Hydrogen treatment reduces the tensile strength of the elastomers by about 5-10% and their elongation by 0-25%, and increases the softness up to about 5%, but at least doubles the ozone resistance, materially increases the sunlight resistance, and improves the aging and corona resistances.

PDL-30118

Burke Research Company, Van Dyke, Mich.
DEVELOPMENT OF PRACTICAL ANTIOZONANTS, by F.C. Bruce and B.P. Hunt.
U.S. Ordnance Corps. Contract DA-20-089-ORD-36531, Report No. 54.
April 1957.

[Antiozinants, research, GR-S rubber, wax]

PDL-30196

Haagen-Smit (Jan W.), South Pasadena, Calif.
OZONE RESISTANT COMPONENTS, . . . SECOND EXPOSURE YEAR, by
John W. Brooks.
Contract DA-04-495-ORD-886, Progress Report 47. [n.d.]

[Tire, ozone resistance, research, rubber]

PDL-30353

Bush (G.F.) Associates, Princeton, N.J.
GFB OZONE DETECTORALARM, MODEL A.1.
[n.d.] [3] 1.

[Ozone, test equipment, commercial, atmosphere]

PDL-30392

Christian, George L.
TRANSPARENT SILICONE RUBBER DEVELOPED.
Aviation Week 66(2):82-84. January 1957.

[Review, windshields, silicone rubber, high temperature, laminates, fluorosilicone rubber, swelling, temperature extremes, seals, hydraulic fluids, oil resistance, fuel resistance]

Two new silicone rubbers now available in limited quantity are: Silastic Type K interlayer, which is completely transparent and Silastic LS-53, a fluorosilicone rubber which performs well as O-ring or other seal material over a temperature range of -80 to 400 F. Silastic LS-53 resists swelling and attack by gasoline, jet fuels, engine oil, and hydraulic fluids.

Silastic Type K replaces the conventional polyvinyl butyral interlayer in the windshields in supersonic aircraft. Windshields made with this type of silastic retain full strength and clarity through the temperature range of -65 to 350 F. Shatter resistance is somewhat lower than that of conventional laminates but the strength of the latter falls off rapidly above 160 F. At 200 F, the new silicone windshield is more than twice as strong. In the uncured stage, the material is a soft, plastic and extremely tacky sheet. It is calendered between layers of polyethylene coated paper. No bonding adhesive is required. When laminated and cured under pressure in either flat or curved 'glazings', Silastic Type K forms a tough, rubbery interlayer with excellent optical properties. Haze and distortion are minimized, and a high order of transmission is obtained over the entire spectrum.

Silastic LS-53 combines the properties of fluorocarbon plastics and silicone rubbers. Although its temperature range is not as wide as some other silicone rubbers, its low swell characteristics in contact with aircraft fluids and lubricants make it suitable as a sealing medium in wheel wells, inspection doors, ducts, diaphragms, boots and aircraft hose. It is more resistant to hydrocarbon fuels and oils than to diester fluids.

PDL-30538

Haagen-Smit (Jan W.), San Gabriel, Calif.
OZONE RESISTANT COMPONENTS, . . . SECOND EXPOSURE YEAR, by
John W. Brooks.
Contract DA-04-495-ORD-886, Progress Report 49. [n.d.]

[Research, rubber, ozone, cracking]

PDL-30558

Haagen-Smit (Jan W.), San Gabriel, Calif.
OZONE RESISTANT COMPONENTS, . . . THIRD EXPOSURE YEAR, by
John W. Brooks.
Contract DA-04-495-ORD-886, Progress Report 50. [n.d.]

[Progress report, rubber, automotive, components, ozone, tests]

PDL-30619 Burke Research Company, Van Dyke, Mich.
DEVELOPMENT OF PRACTICAL ANTIOZONANTS, by F.C. Bruce and B.P. Hunt.
U.S. Ordnance Corps. Contract DA-20-089-ORD-36531, Report No. 55.
May 1957.

[Research, antiozonants, GR-S, rubber, wax, antioxidants, aging]

PDL-30788 U.S. Naval Civil Engineering Research and Evaluation Laboratory,
Port Hueneme, Calif.
PROCEEDINGS OF SYMPOSIUM ON PRESERVATION FOR MOBILIZATION REQUIRE-
MENTS, 23, 24, 25 OCTOBER 1956.
527 p.

[Symposium, vehicles, components, storage, dehumidification, climate, Teflon, coatings, VCI, anticorrosive agents, antiozinants, plastics, metals, rubber, cost, corrosion, slushing compounds, lubricants, ozone cracking]

The main emphasis in this symposium was directed to methods of long term storage of vehicles and accessory components which permit their immediate return to operational status. The papers included deal with dehumidified storage, storage in polyethylene hutments, caves, and mines, ozone deterioration of rubber and antiozinants for its prevention, the use of permanent and removable coatings for the prevention of corrosion, the types of and uses for volatile corrosion inhibitors, the use of Teflon and other fluorocarbon elastomers as coatings and lubricants, and the economic factors involved in long term storage. Also included are a panel discussion and a report of a question and answer period.

PDL-30900 Haagen-Smit (Jan W.), South Pasadena, Calif.
OZONE RESISTANT COMPONENTS, . . . SECOND EXPOSURE YEAR, by
John W. Brooks.
Contract DA-04-495-ORD-886, Progress Report 48. [n.d.]

[Ozone, automotive components, rubber, progress report, ozone cracking, atmosphere]

PDL-30936 Albert, Harry E.
PROTECTION OF RUBBER FROM OZONE BY MEANS OF BIS(2-ALKYL-4-
ISOPROPYLPHENOL) MONOSULFIDES.
U.S. Pat. 2,802,892; August 13, 1957. [3] p.

[Patent, antiozinants, rubber, sulfides, phenols]

PDL-31061 U.S. Atomic Energy Commission. Oak Ridge National Laboratory,
Oak Ridge, Tenn. Chemical Technology Division.
GAMMA RADIATION DAMAGE STUDIES OF ORGANIC PROTECTIVE COATINGS AND
GASKETS, by J.C. Bresee, C.D. Watson, and J.S. Watson.
Report ORNL-2174(Chemistry); Contract W-7405, eng 26. November 1956.

[Atomic radiation, polymers, gaskets, coatings, films, stability, research]

PDL-31131

Haagen-Smit (Jan W.), San Gabriel, Calif.
OZONE RESISTANT COMPONENTS, . . . THIRD EXPOSURE YEAR, by
John W. Brooks.
Contract DA-04-495-ORD-886, Progress Report 51. [n.d.]
[Antiozinants, rubber, weathering, progress report, tires]

PDL-31253

Vacca, G.N. and C.V. Lundberg.
AGING OF NEOPRENE IN A WEATHEROMETER.
Wire and Wire Products 32:418-422, 457. April 1957.

[Research, tests, aging, neoprene, weathering, comparison, jacket, GR-S]

Samples of various types of thin neoprene sheets, neoprene jacket stock, and neoprene jacketed wire were subjected to four series of tests involving exposures in a weatherometer up to 8000 hr, in a 100 C air oven up to 25 days, in an oxygen bomb up to 10 days, and outdoors at Murray Hill, N.J. up to 54 mo. Changes in tensile strength and per cent elongation of the specimens during various periods were measured and are presented in both graphical and tabular forms.

Results indicated that the weatherometer is unable to produce differences significant enough to permit a definite conclusion on the aging effect on different specimens. Thus it is unsuitable for use in estimating service life of neoprene jackets. A reliable criterion of expected service life is obtained in a comparatively short time by the use of an accelerated ozone test in conjunction with a 100 C air oven test. Weatherometer tests appear to be much more useful in evaluating weathering behavior of GR-S jackets.

The weatherometer used was a National X1A accelerated weathering unit using National sunshine carbons and without Corex glass filters. Curved aluminum baffles protected the samples from the direct rays of the carbon arc for a distance of 90°.

PDL-31265

Lundberg, C.V., G.N. Vacca, and B.S. Biggs.
RESISTANCE OF RUBBER COMPOUNDS TO OUTDOOR AND ACCELERATED OZONE ATTACK.
Rubber World 135:699-713. February 1957.

[Research, ozone, cracking, rubber, styrene-butadiene polymers, neoprene, nitrile rubber, Butyl rubber, antioxidants, antiozonants, wax, weathering (natural), weathering (accelerated), comparisons, N,N'-dioctyl-p-phenylenediamine]

Static tests are reported for 80 styrene-butadiene (SBR) and 9 neoprene rubber compounds exposed in Los Angeles, Calif., Murray Hill, N.J. (18 mo), and Yuma, Ariz. (15 mo) and in ozone chambers operated at 100, 110, and 120 F and 25 and 50 ppm ozone concentration. Both hot SBR and cold oil-extended SBR polymers were tested. All contained carbon black; most contained some mineral filler; and some contained a relatively high quantity of asphaltic material. The compositions contained ozone resisting waxes, larger than normal quantities of antioxidants, and antiozonants such as N,N'-dioctyl-p-phenylenediamine and 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline. Another series of tests

involved outdoor exposures at Murray Hill only, together with exposures in the three ozone chambers. Compounds used were 87 additional SBR compositions, 17 natural rubbers, 16 nitrile, and 60 Butyl rubbers. In addition to the formulations described above, some of the Butyl compounds contained a dimethylnaphthalene-formaldehyde condensate.

The series of SBR compounds initially exposed in the summer showed a higher percentage of ozone cracks on exposure in Los Angeles and Yuma than in Murray Hill. When exposure was initiated in November, however, the Los Angeles and Murray Hill exposures gave results similar to those in the earlier Los Angeles exposure.

The ozone chamber operating at 110 F and 25 pphm ozone gave fewer cracked SBR specimens than the chambers operating at 120 F and 25 pphm ozone, and 100 F and 50 pphm ozone. The last two chambers had about the same effect. A greater percentage of cracked specimens was found in 6 mo than in 1 wk old SBR specimens. The results from the 110 F chamber with 6 mo old specimens correlated well with outdoor aging at Los Angeles and Murray Hill; the 120 and 100 F chambers produced more cracked specimens than were obtained outdoors.

The neoprenes, natural rubbers, and nitrile rubbers showed good correlation among ozone chambers and on outdoor exposure. The neoprene compositions, when protected by wax (other than paraffin), remained uncracked in ozone chambers and outdoors. The natural and nitrile rubbers were not resistant. The 2 1/2 and 3% unsaturated Butyl compounds also showed good correlation among chambers and on outdoor exposure. The only uncracked specimens were those containing wax and the N,N'-dioctyl-p-phenylenediamine. The 1% and 2% unsaturated Butyls showed poorer correlation in the various atmospheres than the 2 1/2 and 3% unsaturated Butyls, but were protected by the same combination of agents. Waxes alone also offered some protection against cracking.

Unprotected SBR samples cracked in all chamber and outdoor tests. Six formulations containing 6 to 8 phr wax (12% of all wax-containing compounds) survived all outdoor tests. Higher than normal concentrations of antioxidants such as quinoline derivatives, diphenyl-p-phenylenediamine, and an acetone-diphenylamine reaction product did not protect SBR when used alone, but in 26 compounds (34%) they were effective outdoors when used with wax. Combinations of 3 to 5 phr antioxidant used with 3 to 6 phr wax gave SBR greater ozone resistance than wax alone. N,N'-dioctyl-p-phenylenediamine and wax in ratios of 1 phr to 5 phr or 2 phr to 3 phr were the most reliable antiozonants for protecting SBR compounds against static outdoor ozone cracking.

PDL-31367

Perrott, Walter O.

OZONE RESISTANT TIRES.

U.S. Detroit Arsenal, Center Line, Mich. Laboratories Division.

Report No. 3814 (Final). January 1957.

[Progress report, rubber, tires, ozone resistance, tests]

PDL-31377

Thorp, Clark E.
BIBLIOGRAPHY OF OZONE TECHNOLOGY. VOLUME 1. ANALYTICAL PROCEDURES
AND PATENT INDEX.
Chicago, Ill., Armour Research Foundation. 1954. 209 p.
[Bibliography, ozone, analysis, microbicide]

PDL-31378

Thorp, Clark E.
BIBLIOGRAPHY OF OZONE TECHNOLOGY. VOLUME 2. PHYSICAL AND
PHARMACOLOGICAL PROPERTIES.
Chicago, Ill., Armour Research Foundation. 1955. 160 p.
[Bibliography, ozone, pharmacology, microbicide, toxicology]

PDL-31420

Bergstrom, E.W.
PROTECTION OF RUBBER VULCANIZATES FROM OZONE CRACKING BY EXTERNAL
ANTIOZONANT APPLICATION.
U.S. Arsenal, Rock Island, Ill. Laboratory. Technical Report 56-3158.
November 1956.
[Research, rubber, antiozonants, dioctyl-p-phenylenediamine,
application method, GR-S, nitrile rubber]

The ozone resistance imparted to vulcanizates of unplasticized, oil-extended, or peroxide-cured GR-S, natural rubber, and nitrile rubber by dipping in an antiozonant solution was superior to that imparted by incorporating the antiozonant in the rubber at the time of mixing. The antiozonant used in these studies was a 10 to 50% solution of N,N-dioctyl-p-phenylenediamine in acetone.

Even after aging for 70 hr at 212 F, unplasticized GR-S, oil-extended GR-S, and natural rubber vulcanizates dipped in the antiozonant solution had excellent ozone resistance in accelerated static tests carried out at 100 F in an atmosphere containing 25 and 50 pphm ozone.

In accelerated dynamic ozone exposure tests at 100 F with 15 pphm ozone, dip-coated unplasticized GR-S, and natural and nitrile rubber vulcanizates had excellent ozone resistance. A GR-S vulcanizate treated by dipping resisted cracking for 150 hr compared to 36 hr for a vulcanizate in which 3 parts of antiozonant per 100 parts rubber hydrocarbon (rhc) were incorporated at the time of mixing.

In outdoor dynamic tests, a dip-coated GR-S vulcanizate had better resistance than the same vulcanizate containing as high as 6 parts per 100 rhc added at the time of mixing. Time to first crack was 90 days for a dip-coated specimen and 65 days for one compounded with 6 parts antiozonant.

When an antiozonant is added in the compounding process, it may be adversely affected by reaction with any of the compounding ingredients during curing or it may be solubilized by an oil or plasticizer. When the antiozonant is added by dipping, it cannot affect the physical properties of the rubber by accelerating or retarding the cure.

- PDL-31531 Garvey, B.S., jr.
MATERIALS OF CONSTRUCTION: ELASTOMERS.
Ind. Eng. Chem. 49:1593-1598. September 1957.

[Review, elastomers, rubber, nomenclature, bibliography]
- PDL-31653 Seligman, Kurt L.
FORMATION OF MICROGEL DURING ACCELERATED AGING OF NEOPRENE LATEX.
Ind. Eng. Chem. 49:1709-1712. October 1957.

[Research, neoprene, aging, pH, mechanism, microgel]
- PDL-32076 Haagen-Smit (Jan W.), San Gabriel, Calif.
OZONE TESTING OF RUBBER COMPONENTS AT PASADENA, CALIFORNIA,
INSTALLED ON M-35, 2-1/2 TON TRUCK.
Project MBR-127; Contract DA-04-495-ORD-886. [n.d.]

[Tabulation, antiozonants; rubber, automotive, components,
weathering, California, Butyl, GR-S, neoprene, elastomers, Buna N]
- PDL-32175 Haagen-Smit (Jan W.), San Gabriel, Calif.
OZONE RESISTANT COMPONENTS, . . . THIRD EXPOSURE YEAR, by
John W. Brooks.
Contract DA-04-495-ORD-886, Progress Report 55. [n.d.]

[Progress report, rubber, automotive, components, ozone, tests]
- PDL-32538 U.S. Detroit Arsenal, Center Line, Mich.
SYMPOSIUM ON AUTOMOTIVE RUBBER.
Index of papers presented at Ordnance Tank-Automotive Command
Rubber Symposium, March 28, 1958. 92 p.

[Symposium, rubber, automobiles, tires, stockpiling, storage, Butyl
rubber, Coral rubber, tires, ozone cracking, antiozonants, GR-S,
Buna N, amines, wax, elastomers, urethan]
- PDL-32691 Haagen-Smit (Jan W.), San Gabriel, Calif.
OZONE RESISTANT COMPONENTS, . . . THIRD EXPOSURE YEAR, by
John W. Brooks.
Contract DA-04-495-ORD-886, Progress Report 58. 1958.

[Progress report, automotive, components, ozone, cracking, rubber]
- PDL-32754 Haagen-Smit (Jan W.), San Gabriel, Calif.
OZONE RESISTANT COMPONENTS, . . . THIRD EXPOSURE YEAR, by
John W. Brooks.
Contract DA-04-495-ORD-886, Progress Report 59. 1958.

[Progress report, automotive, components, ozone, cracking, rubber]

PDL-33217

Haagen-Smit (Jan W.), San Gabriel, Calif.
OZONE RESISTANT COMPONENTS, . . . THIRD EXPOSURE YEAR, by
John W. Brooks.
Contract DA-04-495-ORD-886, Progress Report 60. 1958.

[Progress report, rubber, components, ozone resistance, weathering]

PDL-33508

Bergstrom, E.W.
AGING OF UNSTRESSED ELASTOMERIC VULCANIZATES DURING OUTDOOR AND
CONTROLLED HUMIDITY EXPOSURES.
U.S. Arsenal, Rock Island, Ill. Laboratory. Report 58-1808.
July 1958.

[Research, aging, humidity, rubber, butadiene, styrene, isobutylene,
isoprene, acrylonitrile, copolymers, chloroprene, elastomers,
weathering]

This report covers the effects of a long term humidity aging program on the physical properties of vulcanizates based on copolymers of butadiene/styrene, isobutylene/isoprene, butadiene/acrylonitrile, the homopolymer of chloroprene, and natural rubber vulcanizates with and without antioxidant. The vulcanizates were exposed indoors in an unstressed condition for 1, 3, 5, and 7 yr, to 0, 50, and 100 RH, and to a cycle of 1 mo at 0 RH and 1 mo at 100% RH. All of the vulcanizates except, the uninhibited natural rubber, were also exposed outdoors on a rooftop of the Rock Island Arsenal for 6 yr in an unstressed condition.

A statistical analysis of the data obtained from the humidity aging tests showed that relative humidity was not a significant factor in aging. All vulcanizates aged more outdoors than indoors. The hevea and butadiene/styrene vulcanizates showed the greatest differences in amount of deterioration (outdoors vs. indoor) while the isobutylene/isoprene vulcanizates showed the least.

PDL-33631

Haagen-Smit (Jan W.), San Gabriel, Calif.
OZONE RESISTANT COMPONENTS, . . . THIRD EXPOSURE YEAR, FINAL
PROGRESS REPORT, by John W. Brooks.
Contract DA-04-495-ORD-886, Report 61. 1958.

[Progress report, rubber, ozone, cracking, automotive, components]

PDL-33634

Haagen-Smit (Jan W.), San Gabriel, Calif.
OZONE RESISTANT COMPONENTS, . . . FOURTH EXPOSURE YEAR, FIRST
PROGRESS REPORT, by John W. Brooks.
Contract DA-04-495-ORD-886, Report 62. 1958.

[Progress report, rubber, ozone, cracking, automotive, components]

PDL-34959

Haagen-Smit (Jan W.), San Gabriel, Calif.
OZONE RESISTANT COMPONENTS, . . . FOURTH EXPOSURE YEAR.
Contract DA-04-495-ORD-1235, Report 70. 1959.

[Progress report, rubber, automotive, ozone]

PDL-35081

Haagen-Smit, A.J.
RUBBER AND ITS ENVIRONMENT.
Am. Soc. Testing Materials, Spec. Tech. Publ. No. 229:3-10.
1958.

[Symposium, review, rubber, atmosphere, oxidation, light, ozone, contaminants, discoloration, mechanism]

PDL-35089

Veith, A.G.
REPORT ON INTERLABORATORY OZONE TEST PROGRAM OF ASTM COMMITTEE D-11,
SUBCOMMITTEE XV ON LIFE TESTS FOR RUBBER PRODUCTS, 1957.
Am. Soc. Testing Materials, Spec. Tech. Publ. No. 229:113-130.
1958.

[Test, program, ozone, test equipment, comparison, styrene, butadiene, neoprene, butyl, elastomers, reliability]

PDL-35112

Haagen-Smit (Jan W.), San Gabriel, Calif.
OZONE RESISTANT COMPONENTS, . . . FOURTH EXPOSURE YEAR.
Contract DA-04-495-ORD-1235, Report 71. 1959.

[Progress report, rubber, automotive, ozone]

PDL-35303

Meyer, Glen E., F.J. Naples, and H.M. Rice.
HEAT, OZONE, AND GAMMA RADIATION STABILITY OF HIGHLY SATURATED
ADDUCT RUBBER VULCANIZATES.
Rubber World 140:435-438. June 1959.

[Research, elastomers, butadiene, saturation, aging, ozone, temperature, radiation (high energy), comparisons, Butyl, neoprene, rubber, vulcanizates]

Highly saturated (over 80%) methyl mercaptan adducts of emulsion polybutadiene were highly resistant to heat, ozone, and gamma radiation, and the resistance increased with increasing saturation levels. At 300 F in air, the adducts showed better retention of stress-strain properties than neoprene, and the 95% saturated adduct matched the aging properties of resin cured Butyl up to 5 days. At 500 to 600 F, the adducts were far superior to both resin cured Butyl and neoprene. All the adducts tested were extremely resistant to ozone attack. The 95% saturated adducts with no added antiozonant withstood ozone attack for 300 hr under conditions which caused deterioration in neoprene in 1 hr and in Butyl in 20 hr. Both the 88% and 95% saturated adducts exhibited much greater resistance to gamma radiation deterioration than natural rubber. Within the temperature range of -120 to +200 F, the adducts maintained this resistance, whereas that of natural rubber degraded at an increasingly higher rate as the temperature increased.

PDL-35382 U.S. Naval Shipyard, Brooklyn, N.Y. Material Laboratory.
STANDARDIZATION OF PACKAGING MATERIALS FOR SHELF AGING OF NATURAL
AND SYNTHETIC RUBBER MATERIALS (NSS-033-200).
Laboratory Project 5974, Parts 1 and 2, Progress Report 1.
November 1958.

[Progress report, seals, aging, accelerated, temperature, rubber,
elastomers, test, comparison]

PDL-35470 U.S. Naval Shipyard, Brooklyn, N.Y. Material Laboratory.
REPLICA TECHNIQUE FOR EVALUATION OF OZONE DETERIORATION OF RUBBER
AND SYNTHETIC RUBBER.
Laboratory Project 4912-4, Progress Report 1. October 1952.

PDL-35485 Haagen-Smit (Jan W.), San Gabriel, Calif.
OZONE RESISTANT COMPONENTS, . . . FOURTH EXPOSURE YEAR.
Contract DA-04-495-ORD-1235, Report 72. 1959.

[Progress report, rubber, automotive, ozone, cracking]

PDL-35676 Sinnott, R.
THE MECHANICAL PROPERTIES OF SYNTHETIC RUBBERS AT ELEVATED
TEMPERATURES. 1. BUTYL, NEOPRENE AND NITRILE RUBBERS.
Gt. Brit. Royal Aircraft Establishment, Farnborough. Technical
Note. Chem. 1342. December 1958.

[Research, elastomers, Butyl, neoprene, nitrile, temperature,
aging, mechanical properties, tests]

Apparatus was adapted for the measurement of hardness, tensile strength, modulus, and breaking elongation of Butyl, neoprene, and nitrile rubbers at temperatures up to 200 C. High temperatures may change the dimensions of measuring instruments and of measured objects, and thus affect the magnitude of the results. Reproducibility of results is lower when tests are carried out at high rather than room temperature, particularly in measurements of tensile properties at break. This phenomenon is believed to be caused by the influence of increasing heterogeneity in the rubber at high temperature. In preparing samples for high temperature testing, much greater care than usual is necessary in mixing and vulcanizing. A greater number of samples also may be needed to obtain a reliable estimate of results.

The tensile strength of all three rubbers decreases rapidly between 20 and 100 C, and more slowly with a further rise in temperature. Neoprene is most affected, retaining only one eighth of its strength at 100 C. Butyl is affected the least, retaining half its strength. Elongation at break is less influenced than tensile strength by rise in temperature, 50 to 70% of the elongation at 20 C being retained at 100 C and somewhat less at 150 C. The effect of temperature on modulus and hardness is relatively small, a slight decrease between 20 C and 70 C being followed by a slow increase with further rise in temperature. With Butyl rubber, there is a sharp decrease in modulus and hardness between 150 and 200 C.

Tensile properties of Butyl and nitrile rubber are not greatly changed after aging 28 days at 100 C; a slight decrease in tensile strength and a decrease of about one third in breaking elongation occur. In neoprene, there is a moderately rapid increase in tensile strength and a corresponding decrease in elongation at break. Hardness and modulus increase rapidly during the first week and more slowly thereafter. In general, the effects are similar, but more rapid at 125 C. In Butyl rubber, reversion begins to predominate over crosslinking, and after the first few days the rubber softens and becomes less stiff.

The limits of useful service of these rubbers is approached at 150 C. After 2 days, both neoprene and nitrile lose a large part of their rubberlike properties; surface hardening by oxidation is rapid. With Butyl rubber, heat softening again predominates; after 2 wk, this rubber still retains a useful proportion of its original properties. Laboratory aging conditions, it is emphasized, are more severe than those of many service applications.

PDL-35858

U.S. Naval Shipyard, Brooklyn, N.Y. Material Laboratory.
SHELF AGING OF SYNTHETIC AND NATURAL RUBBER MATERIALS;
INVESTIGATION OF.

Laboratory Project 5974, Parts 3 and 4, Progress Report 2.
December 1959.

[Rubber, elastomer, neoprene, aging, temperature, packaging]

PDL-35930

Eynck, John J.
OZONE TESTING OF NEOPRENE COMPOUNDS FOR SAE-ASTM SUBCOMMITTEE IVP4.
U.S. Naval Shipyard, Mare Island, Calif. Rubber Laboratory.
Report 4-50. August 1958.

[Elastomers, ozone, neoprene, test]

PDL-36022

Leyland, B.N. and R.L. Stafford.
AGEING OF RUBBER: EFFECTS OF METAL CONTAMINATION.
Inst. Rubber Ind., Trans. 35:25-44. April 1959.

[Rubber, contaminants, copper, iron, oxidation, oxidationproofers]

The oxidation of raw rubber is promoted strongly by small amounts of copper (30 to 100 ppm), especially when introduced as the salts of weak organic acids. These salts may act as pro-oxidants, increasing the rate of the oxidation but not affecting the nature of the oxidative reaction. Iron in the form of iron stearate, although not as active as copper as a pro-oxidant in raw rubber, could still be a source of serious degradation.

Zinc diethyldithiocarbamate (ZDC) and tetramethylthiuram disulfide (TMT) are effective inhibitors against oxidation by copper contaminants. A nonstaining inhibitor, originally developed for vulcanized compounds, also affords protection against both copper and iron in raw rubber.

In sulfur-vulcanized compounds copper and iron also exert pro-oxidant activity, the relative effects being smaller the greater the oxidizability of the uncontaminated control compound. In these compounds, ferric stearate is as potent as copper stearate in promoting degradation. Although a few conventional antioxidants give fairly good protection against copper contamination in vulcanized rubber, there is a need for even more powerful metal inhibitors which are also good conventional antioxidants. The synergism of selected antioxidants with mercaptobenzimidazole (MBI) is demonstrated in copper-contaminated compounds, leading to the design of improved inhibitors. Some characteristics of a nonstaining inhibiting system of this type are discussed, including its effectiveness in both raw and vulcanized rubber; this affords a means of conferring protection against metal contamination both before and after vulcanization. In vulcanized compounds, such a system gives effective protection against both high and room temperature oxidation.

Sulfurless TMT vulcanized compounds react very differently to metal contamination. In such compounds, copper stearate itself acts as powerful antioxidant whereas ferric stearate still remains markedly pro-oxidant in its effect.

PDL-36169

Tobolsky, A.V. and A. Mercurio.
ON THE CATALYZED OXIDATIVE DEGRADATION OF NATURAL RUBBER NETWORKS.
Am. Chem. Soc., J. 81:5539-5540. November 1959.

[Rubber, oxidation, mechanism, catalysis]

Natural rubber vulcanizates prepared by electron irradiation were subjected to air oxidation in the presence of benzoyl peroxide and tetramethylthiuram disulfide (TMTD) as initiators. With benzoyl peroxide the rate of oxidative chain scission deduced from stress relaxation experiments is essentially the same as the rate of production of radicals from the benzoyl peroxide. This result also has been found in studies of oxidation scission in dilute solutions of natural rubber in benzene. The finding is consistent with the occurrence of chain scission in the termination step of the free radical oxidation. Data on the rate of chain scission observed with TMTD are compared with reported polymerization data using the same initiator. Initiation by this system is best described as a bimolecular reaction between TMTD and substrate (either monomer or isoprene segments in rubber).

Stress relaxation measurements were carried out at a constant extension of about 20%. Benzoyl peroxide tests were carried out for 12 hr at 80 C, and TMTD tests up to 72 hr at 78, 80, and 100 C.

PDL-36197

Thelin, J.H. and A.R. Davis.
COMPARISONS OF ANTIOXIDANT-ANTIOZONANT ACTIVITIES OF SOME PROTECTIVE AGENTS.
Rubber Age (N.Y.) 86:81-85. October 1959.

[Ozoneproofers, oxidationproofers, rubber, elastomers, p-phenylenediamine, phenols]

PDL-36197
(cont.)

Several antioxidants were tested for antiozonant activity and some antiozonants were tested for antioxidant activity. Compounds investigated included a large number of p-phenylenediamine derivatives and phenolic compounds. The additives, usually 3% of antiozonant and 1% of antioxidant, were incorporated in black-loaded natural rubber, black-loaded styrene-butadiene and white-loaded natural rubber. Antioxidant activity was measured by the percent tensile retention after the specimen was exposed to oxygen bomb conditions at 80 C for 48 hr at 300 psi O₂. Antiozonant activity was evaluated by measuring the time taken to produce cracks discernible under a magnification of 7.5 diameters while under 100% elongation at 38 C, essentially method ASTM D-1149-54T.

The best antiozonants in the p-phenylenediamine series were found to be the least active as antioxidants and the best antioxidants were the least active as antiozonants. This behavior is related to the type of substituent, i.e., aromatic or aliphatic-cycloaliphatic, on the nitrogen atoms. Phenolic type antioxidants had no antiozonant activity in loaded stocks.

Antioxidant and antiozonant mechanisms are considered to be completely different. For any given compound high activity against one of the degradative factors, oxygen or ozone, appears to decrease activity against the other factor.

PDL-36198

Ambeland, J.C. and B.W. Habeck.
WING-STAY 100 AS AN ANTIOZONANT.
Rubber World 141:86-96,146. October 1959.

[Elastomers, styrene-butadiene, ozoneproofers, comparison]

Wing-Stay 100, which is described as a mixture of diaryl-p-phenylenediamines, was evaluated as to its effectiveness against ozone. Static and kinetic tests in the laboratory plus tire road tests indicate that this chemical, because of its low volatility and low oxidation rate, exhibits considerable persistence and relatively long lasting protection.

A new visual method of rating cracking due to ozone permits rating of any type sample such as test strip, tire sidewall, or other vulcanized part. A two-part numerical system rates first the amount of cracks, and second the size of cracks. These ratings are then multiplied and the product is designated as the 'Weathering Index'. This may be used readily for charts and graphs.

The antiozonant efficiency of Wing-Stay 100 was compared with several dihydroquinolines and dialkyl-p-phenylenediamines in cold SBR 1500 and oil-extended SBR 1712. Wing-Stay 100 showed particular persistence even in samples oven aged before exposure to ozone or weather. Safety in processing also is claimed. Scorch data indicate that little or no activation occurs from the use of this material.

PDL-36236

Mohawk Rubber Company, Akron, Ohio.
STORAGE LIFE OF UNVULCANIZED RUBBER COMPOUNDS, by Frank M. Johnson.
U.S. Ordnance Corps. Contract DA-33-019-ORD-1890, Final Report.
June 1958.

[Rubber, elastomer, styrene, butadiene, tires, shelf life, aging, temperature, pressure, storage]

A wide variety of unvulcanized tread rubber and tire repair materials were aged at room temperature, 100, 125, 150, and 200 F in an air oven, and plasticity changes and effect on 300% modulus after curing were determined. Base polymer in all tread rubber samples was some type of styrene-butadiene rubber. Tire repair materials were natural rubber.

Prevulcanization, deactivation of curing rate, and stiffening occurred simultaneously during aging at temperatures up to 150 F. At 200 F, prevulcanization was so rapid that trends toward deactivation of the curing system were obscured.

Maximum aging temperature, at which reasonable estimations of probable shelf life can be determined, is in the vicinity of 150 F. Results at 125 F appeared to be somewhat more reliable than those obtained at 150 F, but a longer aging period was required. None of the samples tested failed after 12 mo at 72 to 83 F, but results at 100 F indicated probable failure at 90 F within 12 mo due to prevulcanization. Many samples would have suffered severe loss in curing activity.

The temperature dependence of the reactions appeared to vary widely for different stocks. Deterioration of cure rate apparently was associated with accelerator disappearance or deactivation.

An increased rate of stiffening occurred when specimens were aged under mild pressure to simulate the pressure at the base of a roll or tread rubber during storage.

PDL-36238

Dunn, J.R., J. Scanlan, and W.F. Watson.
STRESS RELAXATION DURING THE PHOTOOXIDATION OF PEROXIDE CROSSLINKED RUBBER.
British Rubber Producers' Research Association, Welwyn Garden City, England. Publication No. 275. [n.d.] [16] p.

[Rubber, light, degradation, mechanism]

PDL-36239

Scanlan, J. and W.F. Watson.
THE INTERPRETATION OF STRESS-RELAXATION MEASUREMENTS MADE ON RUBBER DURING AGEING.
British Rubber Producers' Research Association, Welwyn Garden City, England. Publication No. 277. [n.d.] [16] p.

[Rubber, stress-relaxation, aging, theory]

The validity of earlier assumptions that tension in a stretched rubber strip is proportional to the number of network chains supporting it, and that chains formed during aging do not contribute to the tension at the constant extension were investigated experimentally.

The results presented are analyzed and discussed. It is concluded that deviation of stress-strain behavior of unswollen rubber from the ideal predicted by elasticity theories has negligible effect on interpretation of stress-relaxation data. The independence of rate relaxation at constant extension on initial extension, and other experimental results accord with a two-term form for the strain energy, of which a special case is required by the two-network hypothesis of Andrews et al to deal with bond formation. Neither these nor earlier tests can test more than the general form of the strain-energy expression. Theoretical treatment of a model network in which one chain is broken and one is formed indicates, however, that the rate of stress relaxation is slower than is predicted by the two-network hypothesis.

PDL-36343

Smith, Frank B.
COMPARATIVE PERFORMANCE OF ANTIOZONANTS IN ROAD AND ACCELERATED TESTS IN THE LOS ANGELES AREA.
Rubber World 141:383-391. December 1959.

[Elastomers, rubber, nylon, styrene-butadiene, tires, ozoneproofers, tests, accelerated]

PDL-36348

Cumneen, J.I. and F.W. Shipley.
CIS-TRANS ISOMERIZATION IN POLYISOPRENES. PART 1. IMPROVEMENT OF THE LOW TEMPERATURE PROPERTIES OF NATURAL RUBBER BY REACTION WITH THIOL ACIDS IN SOLUTION AND IN LATEX.
J. Polymer Sci. 36:77-90. April 1959.

[Rubber, temperatureproofing, chemutation]

PDL-36453

U.S. Ordnance Corps.
ORDNANCE MATERIALS HANDBOOK. RUBBER AND RUBBER-LIKE MATERIALS.
Pamphlet ORDP 20-310. December 1956.

PDL-36459

Haagen-Smit (Jan W.), San Gabriel, Calif.
OZONE RESISTANT COMPONENTS, . . . FIFTH EXPOSURE YEAR.
Contract DA-04-495-ORD-1667, Report 79. [n.d.]

PDL-36460

Haagen-Smit (Jan W.), San Gabriel, Calif.
OZONE RESISTANT COMPONENTS, . . . FIFTH EXPOSURE YEAR.
Contract DA-04-495-ORD-1667, Report 80. [n.d.]

PDL-36517

Juve, Robert D. and Frank M. Johnson.
STORAGE STABILITY OF TREAD RUBBER AND TIRE REPAIR MATERIALS.
Rubber World 141:820-826. March 1960.

[Rubber, elastomer, styrene, butadiene, tires, shelf life, temperature, aging, storage, pressure]

PDL-36526

Mandel, J. and others.

MEASUREMENT OF THE AGING OF RUBBER VULCANIZATES.

J. Research Natl. Bur. Standards 63C:141-145. October - December 1959.

[Rubber, aging, temperature, tests, prediction, tensile properties]

A study of aging data in the literature and laboratory measurements indicate that ultimate elongation is the best of the tensile properties for measuring the deterioration of rubber vulcanizates during storage at various temperatures. In all types of rubber vulcanizates, ultimate elongation (strain at failure) decreases during aging; whereas tensile strength and modulus may increase or remain essentially unchanged.

Measurements of ultimate elongation of nitrile rubber vulcanizates were made after various storage periods at 23, 34, 45, 57, 70, 85, and 100 C. Data also are given on an interlaboratory test involving five different rubbers stored at 25, 70, 100, and 121 C. The change in ultimate elongation over prolonged periods of storage cannot be expressed by a simple mathematical equation. However, during most of the useful storage life, the elongation decreases approximately linearly with the square root of time. If the relationship between aging and temperature is known, prediction of shelf aging can be made from tests at two or more elevated temperatures. The Arrhenius equation appears to hold for some rubber compounds; for these compounds an estimate of storage life can be calculated from the equation $E = E_0 - k/\sqrt{t}$ where E is ultimate elongation after aging for time t , and E_0 and k are parameters of the vulcanizate.

PDL-36591

Leeper, Harold M. and Dudley B. Merrifield.

SYNERGISTIC STABILIZER COMPOSITIONS FOR RUBBER COMPRISING AN N-NITROSO AROMATIC AMINE AND AN ALIPHATIC MONOAMINE.

U.S. Pat. 2,930,777; March 29, 1960. [5] p.

[Rubber, elastomers, ozoneproofing, synergism, amines, patent]

PDL-36659

Bergstrom, E.W.

LOSS OF ANTIOZONANT EFFICACY IN BUTADIENE-STYRENE (SBR) RUBBER AFTER SHELF STORAGE.

U.S. Arsenal, Rock Island, Ill. Laboratory. Report 60-487. February 1960.

[Styrene, copolymers, butadiene, storage, elastomers, ozoneproofers, amines]

An investigation was carried out to determine the ozone resistance of (1) antiozonant inhibited SBR vulcanizates which had been stored unstressed indoors and outdoors for various periods of time, and (2) vulcanizates prepared from the same inhibited compounds after storage indoors for various periods of time prior to curing.

Vulcanizates inhibited with N-phenyl-N'-cyclohexyl-p-phenylene-diamine have excellent ozone resistance in accelerated (25 and 50 ppm) ozone tests when the vulcanizates are stressed and exposed to ozone within 3 days from the date of curing. However, the same vulcanizates

have no ozone resistance in accelerated ozone tests after being stored (1) unstressed indoors for 1 wk or longer, and (2) unstressed outdoors for 1 mo or longer.

All antiozonant-inhibited SBR vulcanizates which had been stored unstressed for periods up to 24 and 30 mo both indoors and out had excellent ozone resistance in outdoor tests.

None of the antiozonants studied, when incorporated in camel back stock provided good ozone resistance (both outdoor and accelerated at 25 and 50 pphm) after storage of the camel back for 12 mo. N,N'-di-2-octyl-p-phenylenediamine monooxalate provided good ozone resistance to vulcanizates prepared from stock which was stored uncured as long as 6 mo.

PDL-36731

Murray, R.M.

FACTORS INFLUENCING THE OZONE RESISTANCE OF NEOPRENE VULCANIZATES UNDER FLEXURE.

Rubber Chem. and Technol. 32:1117-1133. October - November 1959.

[Neoprene, elastomer, ozoneproofers, formulation, test]

PDL-36746

Haagen-Smit, A.J., M.F. Brunelle, and J.W. Haagen-Smit.

OZONE CRACKING IN THE LOS ANGELES AREA.

Rubber Chem. and Technol. 32:1134-1142. October - November 1959.

[Rubber, ozone, cracking, California]

Cracking of rubber due to ozone attack was determined in the Los Angeles area by measuring number and depths of cracks produced in standardized bent rubber strips during sheltered outdoor exposure of usually 1 wk. Cracking shows both daily and seasonal variations due to differences in ozone concentration and temperature; it is especially heavy during smog periods.

Ozone concentration reaches a maximum during the day and a minimum at night and is highest during the summer time. Ozone is formed from the action of sunlight on mixtures of organic matter and oxides of nitrogen, common air pollutants in urban areas. The trend of total oxidant concentration of air, determined with potassium iodide, is similar to that of ozone.

In bent strips exposed outdoors for 2, 4, 6, and 8 days, a linear relation was found between cracking depth and exposure time. In greenhouse tests where ozone concentrations are lower than in air, cracking was much less at 17 than at 20 or 23 C; no cracking occurred below 17 C. When air containing 7 ppm ozone was passed for 10 min over rubber strips heated at temperatures increasing from 5 to 40 C, above 18 C crack depth increased as a linear function of temperature.

PDL-36747

Kilbourne, H.W. and others.

CHEMICAL INHIBITION OF OZONE DEGRADATION OF SBR.

Rubber Chem. and Technol. 32:1155-1163. October - November 1959.

[Styrene-butadiene, elastomers, ozone proofers, structure]

PDL-36747
(cont.)

The ozone ratings of standard antioxidant types used in SBR are listed. The 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline and N',N'-disubstituted p-phenylenediamines represent the most active structures. Steric mesomeric and resonance effects are shown to be important in imparting high levels of antiozone activity. When electronegative groups are substituted in an active structure, antiozone effectiveness is greatly reduced. Antiozonant activity is attributed to efficient stopping of ozone-induced free radical chain reactions in the polymeric structure.

PDL-36748

England, W.D., J.A. Krimian, and R.H. Heinrich.
WEATHER AGING OF ELASTOMERS ON MILITARY VEHICLES.
Rubber Chem. and Technol. 32:1143-1154. October - November 1959.

[Elastomers, vulcanizates, tires, ozoneproofer, coatings (organic), storage, Butyl, neoprene, styrene-butadiene, urethane]

PDL-36913

Minnesota Mining and Manufacturing Company, St. Paul, Minn.
Central Research Dept.
ARCTIC RUBBER, by G.H. Crawford and D.E. Rice.
U.S. Dept. of the Army. Contract DA-19-129-QM-1043, Quarterly Progress Report 10. 1960.

[Rubber, temperatureproof, oilproof, fluorine compounds, organic, elastomers, synthesis, technique, progress report]

PDL-37006

Křížek, V. and F. Rybníkar.
MIKROSKOPISCHE IDENTIFIZIERUNG VON AUSBLÜHUNGEN AUF GUMMI
(Microscopic Identification of "Blooming" on Rubber).
Plaste u. Kautschuk 6:113-117. March 1959.

[Rubber, bloom, identification, ageproofers, vulcanizers]

A simple microscopic method is described which permits rapid identification of additives blooming on rubber surfaces. The bloom is dissolved in benzene, the benzene evaporated and the residue mixed with a small amount of a 5% natural rubber solution in benzene. A few drops of this solution placed on a glass slide produces a film showing a characteristic bloom within 0.5 to 3 hr. The bloom is observed under a polarizing microscope. Formation and growth of the bloom can be observed by this method under conditions resembling those in practice. Photomicrographs illustrate characteristic bloom of 21 typical rubber additives.

PDL-37220

Imperial Chemical Industries Limited, London (Inventors: Jack Mitchell Buist and Gwyn Eifion Williams).
PROCESS FOR THE PROTECTION OF RUBBER ARTICLES.
Gt. Brit. Pat. Spec. 815,263; June 24, 1959. 5 l.

[Patent, rubber, elastomers, antioxidants, phenylenediamine]

PDL-37220
(cont.)

Fabricated vulcanized articles of natural rubber or butadiene polymers or copolymers may be protected from aging by applying a solution or dispersion containing 5 to 60% by wt of an N,N'-substituted p-phenylenediamine. The substituted radicals may be alkyl, cycloalkyl, alkylcycloalkyl, aryl, or aryl with one of the before-mentioned radicals as a substituent. A single brush application of 15 to 30 g/sq m is suitable. A microcrystalline wax may be added in amounts up to 200% of the phenylenediamine.

PDL-37524

Harris, James O.
RUBBER HAVING ENHANCED RESISTANT TO DEGRADATION.
U.S. Pat. 2,921,922; January 19, 1960. [3] p.

[Rubber, elastomers, ozoneproofers]

Addition of 0.1 to 5.0% of a 3-aminocarbazole prevents exposure cracking of sulfur vulcanizable natural rubber, and synthetic diene polymers and their copolymers with a minor proportion of a mono-vinyl compound. The amine group on the ring may be unsubstituted or substituted with an alkyl of 1 to 16 carbons, allyl, phenyl substituted lower allyl, or saturated six-membered alicyclic radicals.

PDL-37535

Langshaw, H.J.M.
THE WEATHERING OF HIGH POLYMERS.
Plastics (London) 25:40-45. January 1960.

[Polymers, elastomer, textiles, plastics, degradation, weathering mechanism]

PDL-37692

Dubrovina, G.I.
[AGING OF CABLE RUBBER] (in Russian).
Zhur. Priklad. Khim. 32:2261-2269. October 1959.

[Rubber, aging, insulation, sheathing, cable, foreign]

Cable insulation rubber and cable sheath rubber were aged for 200 days at 80 C and 100 days at 90 C, according to the standard procedure GOST 271-41. On the assumption that aging of rubber is an oxidation process and a first order reaction, measurements of relative elongation (expressed in percent) were used to obtain the reaction kinetics curves. The experimental curves showed deviations from the straight line at the beginning of the aging process and toward its end. Elongation corresponding to the point of inflexion of the curve at the end of the aging period was designated the critical elongation. It was 250 to 350% for insulation rubber and 105% for sheath rubber. The energy of activation, calculated from accelerated aging data, can be substituted in the Arrhenius equation to determine the reaction constant at the temperature of normal aging. This value (corrected for the more rapid change in mechanical properties under normal conditions) can then be utilized to calculate service life and corresponding critical elongations of cable rubbers from their accelerated aging curves.

The values of service life obtained are only approximate, as the rate of aging of rubber depends on many other factors such as construction and nature of the cable, the interaction between the insulation rubber and the sheath material, the migration of rubber components, the relative humidity, and the biological environment. A study of some of these factors showed that copper compounds, formed by the interaction of sulfur from the rubber with the cable metal, activate the aging process of insulation rubber. Thiuram, used in the vulcanization of insulation rubber, migrates into the cable sheath rubber and accelerates its aging. The aging of insulation rubber also can be accelerated by components of other sheath materials, such as copper naphthenate used for impregnating cotton sheathing. The breakdown voltage of the insulation rubber is determined by its moisture absorption, temperature, and by the thickness and water absorption of the sheathing. When insulation rubber enclosed in a rubber sheath was exposed to moisture, its breakdown voltage increased at the beginning, due to absorption of moisture by the sheath, reached a maximum, then began to fall when moisture penetrated through the sheath and was absorbed by the insulation rubber. Measurements of breakdown voltage can be used to determine the maximum permissible time of exposure of rubber to water vapor.

PDL-37832

Ferris, S.W. and J.S. Sweeley.
DEVELOPMENT OF A LOW-TEMPERATURE ANTI-CHECKING WAX.
Rubber Age (N.Y.) 87:642-646. July 1960.

[Elastomers, tires, ozoneproofers, waxes, comparison, temperature]

Eleven commercial anti-checking waxes were added in amounts of 5 and 10 phr to two weather stripping formulations, one a hot styrene base and the other a 25:75 mixture of cold and hot styrene. Compounds were exposed in an ozone chamber with 25 pphm ozone at 0 F and at 120 F, and outdoors (Pennsylvania) for 1 yr. None of the compounds gave complete protection against crack formulation in all three tests. Ozone cabinet exposure at 0 F was more rigorous than outdoor tests. Protection in the two formulations by the different waxes varied greatly.

Data are also given for previous tests in which sixteen wax fractions (10 phr) were tested in the same way in a styrene rubber tire tread compound. Waxes melting in the 100 to 121 F range, whether paraffin or microcrystalline, gave good protection in 0 F cabinet test or outdoors. Waxes melting above 160 F were uniformly bad outdoors; paraffin waxes were superior to microcrystalline. The best overall performance was shown by paraffin waxes melting in the 140 to 150 F range, although no single fraction was satisfactory under all three sets of conditions.

Fourteen wax blends prepared from commercial paraffin and microcrystalline were tested in the formulation based on cold and hot styrene. Seven gave complete protection at 10 phr and four at 7 phr. Protective waxes showed some correlation between melting point and refractive index. All four effective waxes had melting points between 142 and 146 and indexes of 1.422 and 1.436.

One of the four above waxes was added in amounts of 1, 2, and 3 phr to a rubber tire compound (Polysar) and subjected to sidewall cracking tests under severe winter and summer conditions. No cracking was observed with this compound at any of the levels tested, whereas sidewall strip specimens with up to 3 phr of two commercial anti-checking waxes showed cracking after 175 and 42 days, respectively.

The results confirm the difficulty of predicting outdoor performance from ozone cabinet tests. They also show that some rubbers are more difficult to protect than others.

PDL-37926

Murray, R.M. and J.D. Detenber.

A STUDY OF FIRST AND SECOND ORDER TRANSITION IN NEOPRENE.

du Pont de Nemours (E.I.) and Company, Wilmington, Del. Elastomer Chemicals Dept. Contribution 171. September 1960.

[Neoprene, brittleness, temperature]

Neoprene vulcanizates crystallize most rapidly at -12 C. The temperature at which a vulcanizate is crystallized determines the minimum temperature at which it will thaw, the thaw point being approximately 15 C higher than the crystallization temperature over the range studied. Brittleness temperature is not changed as a result of crystallization. Crystallization resistance of the general purpose dry neoprene types increases in the following order: W, WB, WX, GN, GRT, WRT. Depending on the neoprene type, crystallization is retarded by a factor of 5 to 10 by vulcanization. Variation of filler type does not change the crystallization rate appreciably. Crystallization rate is retarded through the use of sulfur, certain resinous type plasticizers, as well as increased state of cure. Ester plasticizers, which depress brittleness temperature and reduce stiffening at low temperatures, increase the crystallization rate considerably and permit crystallization to occur at very low temperatures. Brittleness and 10,000 psi stiffness temperatures are not affected appreciably by neoprene type, state of cure, or amount and type of filler. Glass transition is approximately 12 C lower than the 10,000 psi stiffness temperature and 6 C lower than the brittleness temperature.

PDL-37985

Park, J.D. and J.R. Lacher.

RUBBER RESEARCH: THE SYNTHESIS OF UNSATURATED FLUOROCARBONS.

U.S. Quartermaster Corps. Contract DA-19-129-QM-1263, Progress Report Quarterly No. 8. August 1960.

[Fluorocarbons, synthesis, elastomers, fuelproof, temperatureproof, progress report]

PDL-38218

Miksch, R. and L. Prölss.

EINIGE UNTERSUCHUNGEN ÜBER SCHUTZWACHSE FÜR VULKANISATE (Investigations on Protective Waxes for Vulcanizates).

Kautschuk u. Gummi 13:WT34-WT41. February 1960.

[Rubber, elastomers, vulcanizates, ozoneproof, wax, foreign]

PDL-38311

Akron. University. Institute of Rubber Research.
STRESS RELAXATION AND STRUCTURE OF HIGH TEMPERATURE ELASTOMERS,
by Maurice Morton, V.R. Allen, and R.D. Gates.
U.S. Office of Naval Research. Contract Nonr-2573(00), Technical
Report 4. 1959.

[Rubber, decomposition, theory]

Natural rubber vulcanizates having different types of crosslinks were found to have very different sol vs. degradation relations. Based on this and other factors, it is proposed that the degradation reaction for these vulcanizates is primarily a random chain scission process. Also, in order to explain the difference between the theoretical relation and the experimental results, it is proposed that this scission of chemical bonds is accompanied by the simultaneous release of chain entanglements ("physical" crosslinks). This results in a concurrent crosslink destruction and random chain scission.

A theoretical study of the effect of chain entanglements on the relation between sol formation and network degradation shows that about one chain entanglement per chemical crosslink is sufficient to explain the observed deviation between the theoretical random chain scission relation and the experimental results.

For a linear polymer having a most probable distribution of molecular weights, the soluble fraction of the crosslinked polymer is dependent only on the number of chemical crosslinks per original primary chain. The sol fraction appears to be considerably greater than proposed by theory for natural rubber vulcanizates, and the deviation from theory is dependent on molecular weight of the primary chains. This deviation has again been attributed to the presence of "physical" crosslinks (chain entanglements) and has been used to calculate the number of chain entanglements per chemical crosslink.

In an attempt to verify the proposal that no recombination occurs during degradation in the swollen state, it was shown that recombination increases as swelling decreases.

PDL-38346

Tobolsky, A.V. and A. Mercurio.
OXIDATIVE DEGRADATION OF POLYDIENE VULCANIZATES.
J. Applied Polymer Sci. 2:186-188. 1959.

[Rubber, butadiene, elastomers, oxidation, temperature, mechanism]

PDL-38595

Fogg, S.G. and P.M. Swift.
COMPOUNDING NATURAL RUBBER FOR SERVICE AT LOW TEMPERATURES.
British Rubber Producers' Research Association, Welwyn Garden City,
England. Technical Bulletin No. 4. December 1959.

[Rubber, temperatureproof, cold, formulation]

PDL-38596

Fletcher, W.P. and S.G. Fogg.
COMPOUNDING NATURAL RUBBER FOR HEAT RESISTANCE.
British Rubber Producers' Research Association, Welwyn Garden City,
England. Technical Bulletin No. 3. 1959.

[Rubber, temperatureproof, formulation]

PDL-38716

Deary, W.A.

COMPARISON OF RUBBER AND SYNTHETIC RUBBER TEST METHODS:
VOLUME SWELL.

U.S. Naval Shipyard, Brooklyn, N.Y. Material Laboratory.
Laboratory Project 5948, Final Report. November 1960.

[Rubber, GR-S, neoprene, nitrile, elastomers, swelling, oil, test, comparison]

Volume swell characteristics of Hevea, butadiene-styrene, neoprene and paracril (nitrile) stocks representing a broad range in degree of swell were determined by a British (B.S. 903, Sections 27.1 and .2 of 1950) and an American method (FTMS No. 601, Method 6211 of 12 Apr 1955). Common immersion medium was an ASTM No. 3; high swelling oil at 158 ± 2 F. The methods were found to be interchangeable as shown by empirical linear equations defining the relationship between the volume swell values. The British method is preferred as the values represent equilibrium conditions. In the American method, the volume swell may represent that occurring during a rapid increase in swell, and precautions must be taken to assure that the immersion period is exactly the same in all tests.

PDL-38721

Boguslavskii, D.B., B.P. Tikhomirov, and V.C. Epshtein.

[DETERMINING THE NATURE OF THE DETERIORATION OF RUBBER-CORD SYSTEMS] (in Russian).

Kauchuk i Rezina 19(1):51-53. January 1960.

[Tire cord, tests, adhesion, elastomers, isotopes]

Radioactive isotopes makes it possible to determine where the actual splitting of rubber-cord products takes place. The method consists in adding a radioactive compound such as calcium strontium oxalate (containing strontium-90) to the binder, impregnating cord fibers with the binder, drying, and determining their radioactivity. The radioactive cord is then used in the preparation of vulcanized rubber-cord samples. The two layers are separated mechanically and the radioactivity of the rubber is determined and expressed as percentage of the cord activity. An alternate method consists in introducing the labeled compound into the rubber, and impregnating the cord with nonradioactive binder. In this case, the radioactivity of the cord is expressed, after separation of the layers, as the percentage of rubber radioactivity.

The two procedures were applied to samples prepared from 50-D cord and butadiene or nitrile rubbers. Binders were latex SKS 30 (a divinyl-styrene copolymer), latex SCS 30 containing protein or 6 to 18% resorcinol-formaldehyde resin, and a carboxylated latex containing resorcinol-formaldehyde resin. The relative radio-activities of the rubber and cord layers indicated that in samples bonded with latex SKS 30 or with latex SKS 30 containing protein, splitting occurs at the rubber-binder boundary and is accompanied by a partial degradation of the binder. When the binder film has high tensile strength, as in samples bonded with SKS 30 latex containing resorcinol-formaldehyde resin or with the carboxylated latex, degradation of the binder,

so-called cohesive degradation, is considerably reduced. If at the same time the adhesive strength is increased, as in samples bonded with latices containing a high percentage of resorcinol-formaldehyde resin, the splitting occurs along a line in the rubber layer.

PDL-38737

British Rubber Producers' Research Association, London (Inventors: J.I. Cunneen, W.P. Fletcher, A.N. Gent, and R.I. Wood).
IMPROVED DERIVATIVES OF NATURAL OR SYNTHETIC RUBBER OR OF GUTTA PERCHA AND THE MANUFACTURE THEREOF.
Gt. Brit. Pat. Spec. 820,261; September 1959. 4 1.

[Rubber, elastomers, temperature, crystalproofing]

The crystallization resistance at low temperatures of natural and synthetic rubber and gutta percha is greatly improved by incorporating a compound containing a thiol acid group. Suitable compounds are thiol naphtholic acid and mono; di- and trichloro-thiolacetic acid. The combined thiol acid in the derivative should be less than 5% by wt of the rubber.

PDL-38921

Hunter, B.A. and others.
STYRENE-BUTADIENE RUBBER (SBR): IMPORTANT STABILITY FACTORS.
Inst. Rubber Ind., Trans. 35:121-143. August 1959.

[Styrene-butadiene, elastomers, oxidationproofing]

PDL-38973

McHenry, W. Dennis.
A RADIOMETRIC METHOD FOR DETERMINING THE VOLATILE LOSS AND MIGRATION OF ORGANIC ADDITIVES IN VULCANIZATES.
U.S. Arsenal, Rock Island, Ill. Laboratory. Report 60-2713.
September 1960.

[Elastomer, styrene-butadiene, vulcanizates, temperatureproofing, pentaerythritol, cadmium compound (organic), barium compound (organic), migration, volatility, radioisotope, tracer, technique]

PDL-39012

Lubchanskaia, L.I. and A.S. Kuzminskii.
[DESTRUCTION OF MOLECULAR CHAINS AND BREAKDOWN OF TRANSVERSE BONDS DURING THE AGEING OF VULCANIZATES] (in Russian).
Doklady Akad. Nauk SSSR 135:1436-1438. December 1960.

[Rubber, elastomers, aging, mechanism]

The kinetics of the chemical relaxation process in natural and butadiene rubber vulcanizates with predominantly mono- and polysulfide crosslinks were studied as an approach to the mechanism of aging. Using a specially designed apparatus, the axial compression relaxometer, deformation of the samples was kept constant at 30% compression, the temperature at 100 C. To eliminate physical relaxation, the compressed samples were kept for two days at room temperature prior to aging.

The curves obtained for vulcanizates with predominantly monosulfide links corresponded to a first order reaction. The ratio of the reaction constant for the natural rubber to that of the butadiene rubber vulcanizate was 8:1, i.e., corresponding approximately to the ratio of the oxidation rates of the polymer chains. In vacuum rates, were reduced for both vulcanizates. In those with predominantly polysulfide crosslinks, the chemical relaxation process became exponential only after a decrease of the stress to about 50% of the initial value. In the initial stage, the reaction rates were approximately equal for the two rubbers; in the second stage the rate for natural rubber was higher than that for butadiene by about 20%, and was not affected by the presence of oxygen. The rate of chemical relaxation of natural rubber with polysulfide crosslinks was about 20 times that with monosulfide links.

Results show that the aging of rubber vulcanizates involves two competing reactions: breaking of crosslinks, and oxidative degradation of the polymer chains. In vulcanizates with strong (monosulfide) crosslinks, the chemical relaxation is determined by the oxidation rate of the polymer chains, and depends on the nature of the polymer and the concentration of oxygen. When the vulcanizate structure comprises mainly the weak polysulfide crosslinks, the rate of thermal breaking of these links exceeds the rate of oxidation of the polymer chains, and depends on the nature of the polymer and the concentration of oxygen. When the vulcanizate structure comprises mainly the weak polysulfide crosslinks, the rate of thermal breaking of these links exceeds the rate of oxidation of the polymer chains, and becomes the determining factor of the rate of aging.

PDL-39160

Braden, M. and A.N. Gent.

THE ATTACK OF OZONE ON STRETCHED RUBBER VULCANIZATES. PARTS 1 AND 2. Rubber Chem. and Technol. 33:1142-1165. October - November 1960.

[Rubber, elastomers, ozone, stress, cracking]

An intensive study was made of: (1) the rate, and the factors determining the rate of propagation of single cuts through thin rubber strips in atmospheres containing ozone; and (2) the conditions necessary for a crack to form or, being formed, to grow. Tests covered a wide range of natural and synthetic vulcanizates.

It is shown that a well-defined rate of cut growth may be determined which is characteristic of growth through the bulk, and substantially independent of the applied tensile stress when this exceeds a critical value necessary for growth to occur at all. The effects of polymer employed, vulcanization system, degree of crosslinking, and presence of fillers and plasticizers on the characteristic rate are examined. Effects of temperature in the range 2 to 80 C and ozone concentration from 0.2 to 2.5 mg/liter are also studied. It is concluded that in highly reactive polymers the rate of advance is determined principally by the rate of incidence of ozone molecule and, for relatively viscous polymers, by the restricted mobility of polymer chains. Effects of degree of crosslinking and method of vulcanization seem secondary; the presence of fillers is negligible.

It is proposed that a characteristic value of the tensile stress at the tip of an initial cut or surface flaw is necessary for growth to occur. This criterion is shown to predict the observed dependence of the applied stress required for crack growth on the length of an initial cut and on the surface smoothness of uncut test pieces. The number of cracks formed in an exposed edge is also shown to accord with the proposed criterion. For vulcanizates of differing stiffness, the appropriate criterion is the stored elastic energy. The critical value is similar for a number of different polymers, and largely unchanged by plasticization, temperature change from 20 to 50 C, and change in ozone concentration. For initial flaws consisting of sharp razor cuts, energy required for propagation is about 60 erg/sq cm of newly formed surface.

PDL-39332

Kazak, T.S. and M.F. IArmolenka.

[KINETICS OF THE CONSUMPTION OF THE INHIBITOR IN THE OXIDATION OF RUBBER BY OXYGEN] (in White Russian).

Akademiia Navuk BSSR, Minsk. Vestsi. Seryia Fizikatekhnichnykh Navuk No. 4:42-46. 1959.

[Rubber, oxidationproofing, decomposition, temperature, rate, foreign]

Natural rubber was extracted with methanol and acetone to remove traces of amines, dissolved in benzene, precipitated with methanol, dried in vacuo, and dissolved in benzene to give a concentration of 2.6%. Portions of the benzene solution, with or without the addition of 1 to 3 millimoles of an antioxidant per 1 mole rubber, were poured on weighed glass plates, the solvent allowed to evaporate, and the plates with the adhering rubber films were weighed and placed in an atmosphere of oxygen at 110, 120, and 130 C. Antioxidants were oxynone (2,4-diaminodiphenylamine) and chrysoidin (2,4-diaminoazobenzene). The course of oxidation was followed by determinations of oxygen consumed and the concentration of the antioxidants in the rubber films (for oxynone by extraction with acetone, and for chrysoidin by extraction with methanol).

Both inhibitors considerably prolonged the induction period and reduced the consumption of oxygen. The length of the induction period was determined by the nature of the inhibitor and by the temperature. Thus, at 120 C, the induction period was 21.5 hr, in the presence of chrysoidin, and 40 hr in the presence of oxynone. In the presence of oxynone, it was 82 hr at 110 C, and 12 hr at 130 C. The induction period in control samples ranged from less than 1 hr to 4 hr, and was little affected by temperature. The concentration of oxynone and chrysoidin in the rubber films decreased steadily during exposure to oxygen, including the induction period. The rate of consumption of the inhibitors increased with temperature. When added in amounts of 2 millimoles per mole rubber, the inhibitors were consumed within 14 hr at 130 C, and within 60 hr at 110 C. When the rubber samples were placed in an atmosphere of carbon dioxide, only a slight decrease in the concentration of the inhibitors was observed, due apparently to the presence of occluded oxygen.

The addition of 0.03% of an oxidation accelerator, such as manganese stearate, considerably reduced the induction period (to 4 hr at 110 C), and increased the rate of consumption of the antioxidants.

PDL-39384

British Rubber Producers' Research Association, London
(Kalyanaramaiyer Chandrasekaran)
IMPROVEMENTS IN THE PRESERVATION OF LATEX.
Gt. Brit. Pat. Spec. 821,872; October 14, 1959. 5 l.

[Latex, rubber, storageproofers, ammonia, selenium compounds
(organic), patent]

Addition of a selenium dialkyl dithiocarbamate, e.g., selenium diethyl dithiocarbamate or selenium dimethyl dithiocarbamate permits reduction of the ammonia preservative level in Hevea latex concentrates to as little as 0.15%. In general, ammonia requirement ranges from 0.15 to 0.25% with the selenium dialkyl dithiocarbamate at 0.04 to 0.2%. If mechanical stability equal to that afforded by 0.7% ammonia is required, 0.01 to 0.1% of an anionic surfactant such as an ammonium soap, e.g., ammonium laurate, also should be added to the ammoniated latex before or after concentration.

PDL-39580

Minnesota Mining and Manufacturing Company, St. Paul, Minn.
Central Research Dept.
ARCTIC RUBBER, by D.E. Rice and G.H. Crawford.
U.S. Dept. of the Army. Contract DA-19-129-QM-1684, Quarterly
Progress Report 1. November 1960.

[Progress report, elastomer, temperatureproof, synthesis,
chemicalproof, fluorine compound (organic)]

PDL-39581

Haagen-Smit (Jan W.), San Gabriel, Calif.
OZONE RESISTANT COMPONENTS, . . . SIXTH EXPOSURE YEAR.
Contract DA-04-495-ORD-1969, Report 89. [n.d.]

[Progress report, ozone, rubber, elastomers, test, protracted,
cracking, automobile]

PDL-39582

Haagen-Smit (Jan W.), San Gabriel, Calif.
OZONE RESISTANT COMPONENTS, . . . SIXTH EXPOSURE YEAR.
Contract DA-04-495-ORD-1969, Report 90. [n.d.]

[Progress report, ozone, rubber, elastomers, test, protracted,
cracking, automobile]

PDL-39639

Minnesota Mining and Manufacturing Company, St. Paul, Minn.
Central Research Dept.
ARCTIC RUBBER, by G.H. Crawford, D.E. Rice, and W.J. Fraser.
U.S. Dept. of the Army. Contract DA-19-129-QM-1043, Research
Report. [n.d.]

[Progress report, elastomer, temperatureproof, fluorine compounds
(organic), polymers, synthesis]

PDL-39677 Haagen-Smit (Jan W.), San Gabriel, Calif.
OZONE RESISTANT COMPONENTS, . . . SIXTH EXPOSURE YEAR.
Contract DA-04-495-ORD-1969, Report 91. [n.d.]

[Ozone, cracking, automotive, components, elastomers, rubber, test, progress report]

PDL-39794 HOW GOOD ARE ENVIRONMENTAL TESTS FOR ELASTOMERS.
Materials in Design Eng. 53(4):124-127. April 1961.

[Elastomers, tests, review, temperature, weathering, aging, ozone, corona, oil, water]

PDL-39799 Edwards, D.C. and E.B. Storey.
A QUANTITATIVE OZONE TEST FOR SMALL SPECIMENS.
Chemistry in Canada 11(11):34-38. November 1959.

[Elastomers, ozone, test]

Effect of ozone on rubber vulcanizates is determined simply and rapidly by measuring movement at the junction of two identical specimen strands tensed in series, with one strand exposed to ozone and the other strand shielded. The test rack has two fixed grips 6.75 in. apart. One end of each T-50 specimen is fixed in a grip; the other ends are joined by a floating grip at 100% elongation. With one specimen sealed in a polyethylene sleeve, the rack is exposed to 25 ± 5 pphm ozone at 120 F. A pointer carried on the floating grip indicates movement to the nearest 0.25 mm on a graph paper scale. Zero is read after allowing 1 hr for equilibration. Subsequent pointer indications are read every 24 hr.

Pointer movement is not a direct measurement of any simple property. It is influenced by the stress-strain properties of the particular vulcanizate, and by the erratic nature of the cracking. Since cracking tends to greater irregularity with time, ozonation in terms of crack depth is more surely determined during the earlier stages of cracking, i.e., at 100 to 125% specimen elongation.

Tests on 'hot' and 'cold' SBR vulcanizates containing 0, 0.5, 1.0, and 2.0 parts antiozonant show the hot SBR compounds much more resistant to ozone at all antiozonant levels. The sensitivity of the method also serves to determine the effect of polymer unsaturation on ozone resistance of butyl vulcanizates.

PDL-39807 Ermolenko, N.F. and T.S. Kazak.
[KINETICS OF OXIDATION OF NATURAL RUBBER IN THE PRESENCE OF INHIBITOR OXYNONE] (in Russian).
Akademiia Navuk BSSR, Minsk. Doklady 3:442-444. November 1959.

[Rubber, oxidationproofing, mechanism]

Thin films of natural rubber on glass were exposed to oxygen under various conditions. Addition of 1 millimole Oxynone (2,4-diaminodiphenylamine) per mole rubber lengthened the induction period

at 120 C to 5 3/4 hr; to 38 hr at 3 millimoles. The oxidation of inhibited rubber was temperature dependent: with 0.2% Oxynone, the induction period was 82 hr at 110 C; 12 1/2 hr at 130 C. During oxidation, the Oxynone content decreased at a rate inversely related to the initial level.

These and previous results indicate a complex oxidative reaction. Such factors as temperature, irradiation, oxygen level, and the presence of an inhibitor or initiator can either inhibit or accelerate the reaction. Depending on conditions—especially on its concentration—one compound may either inhibit or accelerate oxidation. The inhibitor appears to take part in the reaction, and to protect the active centers of the rubber macromolecule from oxidation by a process of solvation. Inhibitor loss during oxidation remains unexplained; radicals formed from the hydrocarbon macromolecule during oxidation possibly may react with the radicals of the inhibitor to yield inert products.

PDL-39883

U.S. Naval Shipyard, Mare Island, Calif. Rubber Laboratory.
EFFECT OF SHELF AGING ON MIL-P-5516 O-RINGS.
Report 92-7. January 1961.

[Elastomer, gasket, storage, aging, shelf life, mechanical properties, progress report]

PDL-39957

Dunkel, Walter L., Robert F. Neu, and Richard R. Phelan.
METHOD FOR IMPROVING THE OZONE RESISTANCE OF STEAM CURED BUTYL RUBBER.
U.S. Pat. 2,974,113; March 7, 1961. [3] p.

[Elastomers, butyl, ozoneproof, process, patent]

Ozone resistance of butyl rubber products is greatly increased by pre-cure dipping in an agitated aqueous slurry consisting of 5 to 50% by wt of one or more accelerators, selected from the group, tetramethylthiuram disulfide, tellurium diethyldithiocarbamate, zinc dibenzylthiocarbamate, and sulfur.

Extrusions or other forms from normal formulations are coated with the slurry by 0.1 to 10-min dipping and cured by any regular method. Steam curing at 100 to 400 F for 1 to 600 min is preferred. Curing under a layer of accelerators increases crosslinking of surface double bonds, and antiozonation is effected without tendency to stain. Particular applications cited are weather-seals, garden hoses, and cable insulation. The technique is applicable to all rubbers, but is less beneficial to high-unsaturation polymers having many reactive double bonds.

PDL-40210

Steele, Doris V. and H.E. Mathews, jr.
DEVELOPMENT OF AN OZONE RESISTANT SYNTHETIC RUBBER COMPOUND FOR LOW TEMPERATURE SERVICE.
U.S. Naval Ordnance Laboratory, White Oak, Md. NAVORD Report 6241.
December 1958.

[Elastomer, ozoneproof, temperatureproof, formulation, polymer, styrene, butadiene, mechanical properties, tests]

PDL-40215

Smith, Thor L. and Paul J. Stedry.
TIME AND TEMPERATURE DEPENDENCE OF THE ULTIMATE PROPERTIES OF AN
SBR RUBBER AT CONSTANT ELONGATIONS.
California Institute of Technology, Pasadena. Jet Propulsion
Laboratory. Technical Report 32-36. September 1960.

[Elastomer, styrene, butadiene, polymer, mechanical properties,
stress, temperature]

PDL-40238

Amberg, L.O. and A.E. Robinson.
ETHYLENE-PROPYLENE RUBBER.
Ind. Eng. Chem. 53:368-370. May 1961.

[Ethylene-propylene, elastomers, ozoneproof, weatherproof, tires]

Data are presented on typical ethylene-propylene copolymers containing 60 to 70 mole % ethylene, with 30 to 45 Mooney viscosity (ML₄, 212F), and 0.87 sp gr. Ozone resistance is outstanding; static and flexed specimens are unaffected after 1 yr at 50 ppm. Aging resistance tests show no serious deterioration after 168 hr at 250 F. Most of its strength is lost after 72 hr at 400 F; progressive softening and embrittlement inward from the surface suggests preventable oxidative deterioration. Deterioration is rapid at 500 F. Solvent resistance is comparable with other hydrocarbon rubbers. Heat build-up of tread-type compounds is a function of modulus, and low temperature flexibility is intermediate between those of SBR and natural rubber.

The relatively low volume-cost, light color, chemical stability, and resistance of ethylene-propylene rubber to ozone, weathering, soiling, and abrasion promise success in such applications as tires, mechanical goods, belting, wire coating, household items, and shoe soles and heels.

PDL-40288

Minnesota Mining and Manufacturing Company, St. Paul, Minn.
Central Research Dept.
ARCTIC RUBBER, by D.E. Rice.
U.S. Dept. of the Army. Contract DA-19-129-QM-1684, Quarterly
Progress Report 2. February 1961.

[Elastomer, temperatureproof, chemicalproof, fluorine compounds
(organic), synthesis, progress report]

PDL-40379

American Society for Testing Materials, Philadelphia, Pa.
REPORT OF COMMITTEE D-11 ON RUBBER AND RUBBER-LIKE MATERIALS.
1961 Preprint 43. 44 p.

[Rubber, elastomer, standards, specification, test, analysis,
polymer, ageing, weathering, seal, adhesion]

PDL-40409

Anderson, H.H.
COMPOUNDING FOR PROTECTIVE MASKS.
Proceedings Sixth Joint Army, Navy, Air Force Conference on
Elastomer Research and Development, Vol. 2, p. 552-564.
October 1960.

[Rubber, ozoneproofing, mechanical properties, masks, formulation]

PDL-40411

Montermoso, J.C., C.B. Griffis, and Angus Wilson.
PROPERTIES OF VULCANIZED NITROSO RUBBER.
Proceedings Sixth Joint Army, Navy, Air Force Conference on
Elastomer Research and Development, Vol. 2, p. 672-677.
October 1960.

[Elastomers, fluorocarbons, nitroso compounds, vulcanizate,
physical properties, chemical properties, processing]

PDL-40446

Ecker, Ruprecht.
BESTIMMUNG DES ALTERUNGSVERHALTENS VON WEICHGUMMI (Aging Tests
for Rubber).
Arch. Tech. Messen, Lfg. 289:31-34. February 1960.

[Rubber, elastomers, aging, tests, foreign]

PDL-40484

Phoenix Gummiwerke Aktiengesellschaft, Hamburg-Harburg, Germany
(Inventors: Walter Stegemann, Heinz Esser, and Gottfried Reuter).
ALTERUNGSSCHUTZMITTEL (Additives for Protecting Rubber and Synthetic
Resins Against Aging).
Ger. Pat. 1,054,700; April 9, 1959. [2] 1.

[Elastomers, oxidationproofers, patent, foreign]

Aging of natural and synthetic rubber and plastics is effectively counteracted by the reaction products of aliphatic azo or hydrazine compounds with aromatic compounds. For example 1% (based on natural rubber) of the reaction product of azodicarbonic acid methyl ester with benzaldehyde is mixed with (parts): 100 smoked sheet, 3 mineral oil, 30 activated silicic acid, 10 titanium dioxide, 10 silica, 5 activated zinc oxide, 1 mercaptobenzothiazyl disulfide, 0.3 diphenylguanidine and 2.5 sulfur. After 7 days of Bierer-Davis aging the vulcanizate showed the following mechanical properties: breaking strength, 160 kg/cm²; breaking elongation, 580%; Shore hardness, 44; and elasticity (20 C), 72%.

PDL-41367

Bergstrom, E.W.
AGING OF ELASTOMER VULCANIZATES AT TEMPERATURES UP TO 900°F.
U.S. Arsenal, Rock Island, Ill. Laboratory. Report 61-543.
February 1961.

[Elastomers, high temperatures, silicone fluorocarbons]

PDL-41367
(cont.)

Properly compounded isobutylene/isoprene vulcanizates showed good heat resistance for at least 28 days at 300 F. Certain silicone and vinylidene fluoride/hexafluoropropylene vulcanizates had good retention of physical properties after 28 days at 500 F or 7 days at 600 F. All vulcanizates had poor heat resistance when aged at 700, 800, and 900 F. A vinylidene fluoride/hexafluoropropylene vulcanizate did, however, have measureable physical properties after 5 hr at 700 F, 10 min at 800 F, and 1 min at 900 F.

Certain silicone and vinylidene fluoride hexafluoropropylene vulcanizates had better retention of physical properties when aged in a circulating air oven than when aged in test tubes. Ferric oxide improved the heat resistance of silicone vulcanizates at 500 and 600 F, especially when these were test tube aged.

PDL-41374

Minnesota Mining and Manufacturing Company, St. Paul, Minn.

Central Research Dept.

ARCTIC RUBBER, by D.E. Rice.

U.S. Dept. of the Army. Contract DA-19-129-QM-1684, Quarterly Progress Report 3. May 1961.

[Fluorocarbons, synthesis, temperatureproof, chemicalproof, progress report]

PDL-41491

Dunn, J.R.

THE OXIDATIVE AGING IN ULTRAVIOLET LIGHT OF DICUMYL PEROXIDE VULCANIZATES OF NATURAL RUBBER IN PRESENCE OF VARIOUS ANTI-OXIDANTS.

J. Applied Polymer Sci. 4:151-158. 1960.

[Rubber, ultraviolet, oxidationproofers, mechanism]

Oxidative degradation of dicumyl peroxide vulcanized natural rubber at wavelengths of 300 m μ and above was studied by the stress relaxation technique. Substituted naphthylamines and p-phenylenediamines initially photosensitize the degradation of the vulcanizates, but subsequently give rise to colored products which act as anti-oxidants. Since no increases in permanent set after aging is evident, crosslinking cannot be considered an important factor in protection by amines. The amount of permanent set is dependent only upon the extent of degradation. Inhibitory effect increases as amine concentration increases, but this protective action is not due to network formation. Completely hindered phenols have been shown to be powerful antioxidants; nonhindered phenols are not good antioxidants against light. An ultraviolet absorber with a hindered phenol gives excellent protection which is only fully developed when some of the phenol has been oxidized to a colored compound. Behavior of phenols depends markedly upon the position and nature of the substituent groups particularly the ortho position. Many dithiocarbamates, dithiophosphates, and xanthates protect against light, but their effect is short-lived except for nickel and chromium isopropylxanthates. Their stability is attributed to their action as both ultraviolet absorbers and

antioxidants. Since the addition of ultraviolet absorbers to the nickel and chromium xanthates does not further increase their effectiveness, the combination of a hindered phenol and an ultraviolet absorber is the most potent protective agent against light for incorporation into translucent rubber vulcanizates.

PDL-41519

Cook, A.S.

THE SHORT-TERM PRESERVATION OF NATURAL LATEX.

Rubber Research Inst. Malaya, J. 16:65-86. 1960.

[Rubber, latex, bacteria, toxic]

The preservative effect on various types of natural rubber latex of alkalis, sequestering agents, bactericides and combinations of these are discussed. Formaldehyde was the most effective single chemical; at a level of 0.05% it maintained many latices in liquid condition for 2-3 days. The pH was not affected and no extra acid was required for production of dry rubber by acid coagulation. Preservation was influenced by the type of latex, by weather and other ecological conditions, and especially by wintering of the trees.

The quantities of sodium sulfite, sodium metasilicate, ammonia and formaldehyde required for effective preservation (for smoked sheet production) of latex up to 6 pm on the day of tapping were determined. Formaldehyde appeared to be the most useful. For the production of sheet from latex preserved for 24 hrs, 0.05% formaldehyde plus 0.1% sodium metasilicate was the cheapest and most effective combination.

PDL-41720

Socfin Company Limited, Kuala Lumpur, Malaya (Inventors:

Pierre Robert Gyss, Yezhuveth Bhaskara Menon, and Chan Shee Peng).

IMPROVEMENTS IN METHODS OF PRESERVING LATEX.

Gt. Brit. Pat. Spec. 856,055; December 14, 1960. 5 l.

[Rubber, latex, storageproof, bacteria, toxic, patent]

PDL-41763

Chenicek, Joseph A. and William L. Cox.

PRODUCTION OF A CONCENTRATE OF DIMETHYL ETHERS OF 5-ALKYLPYROGALLOLS.

U.S. Pat. 2,964,569; December 13, 1960. [4] p.

[Patent, ozoneproof, discolorationproof, rubber, synthesis]

PDL-41783

Bruce, F.C. and others.

DEVELOPMENT OF OZONE RESISTANT POLYMERS WITH LOW HYSTERESIS.

Burke Research Company, Van Dyke, Mich. Contract DA-20-018-ORD-17071; Report No. 11. October 1960.

[Elastomers, polymers, extenders, vinyl resin, styrene, butadiene, tire, ozoneproof, synthesis, progress report]

PDL-41810

Akron. University. Institute of Rubber Research.
STRESS RELAXATION AND STRUCTURE OF HIGH TEMPERATURE ELASTOMERS,
by K.W. Scott and others.
U.S. Office of Naval Research. Contract Nonr 2573(00), Final
Report. 1960.

[Elastomer, rubber, structure, stress]

Sol-gel relations in natural rubber vulcanizates were studied both during network formation and degradation. Experimental values obtained during network formation, using swelling measurements to determine crosslink density, deviated markedly from theory, both as to magnitude and in unexpected dependence on primary chain length. This deviation was shown to be due to 'physical' crosslinks, resulting from chain entanglements trapped during network formation. The total number of elastically effective chain entanglements per unit volume and also the effectiveness of a chain entanglement were a function of the concentration of 'chemical' crosslinks.

The theoretical expressions of Horikx for network degradation were modified to include the effect of chain entanglements. Based on this modified theory, it was concluded that the thermal degradation of many vulcanizates of natural rubber occurs by random scission of network chains. A similar type of degradation was found in Viton A elastomer when vulcanized by amines.

PDL-41813

Zuev, Yu. S. and V.F. Malofeevskaya.
[CHEMISTRY OF OZONE CRACKING OF RUBBER AND THE ACTION OF ANTI-
OXIDANTS] (in Russian).
Nauch.-Issledovatel.' Inst. Rezin. Prom. Trudy No. 6:27-53. 1960.

[Rubber, stress, ozone, cracking, mechanism, ozoneproofers, foreign]

The cracking of rubbers subjected to stress and exposed to air can be counteracted by (1) reduction of the stress by physical means such as insulation of rubber surfaces, and (2) reduction of the interaction between ozone in the air and the polymer by chemical methods, e.g., adding antioxidants to the rubber. The reactions of ozone with simple olefins, rubbers in dilute solutions, nonstressed rubbers, and stressed vulcanizates in the absence and in the presence of inhibitors are considered.

The reaction between ozone and unsaturated compounds consists essentially in the formation of ozonides, in breaking carbon-to-carbon double bonds, and formation of carbonyl groups. Anomalous reactions in which more ozone is added than needed to saturate the carbon-to-carbon double bonds occur when electrophilic polar groups are substituted in the vicinity of the double bonds. In some instances, ozone may act as an oxidation catalyst. The mechanism of ozonization of rubbers in dilute solutions is the same as that of simple olefins, and irrespective of the structure of the polymer, results in its degradation. The relative resistance to ozone of certain rubbers can be related to their low degree of unsaturation or to the presence in their molecules of chlorine atoms which polarize the carbon-to-carbon double bond. On nonstressed vulcanizates, sulfur crosslinks which

are less reactive than carbon double bonds, do not appear to affect the mechanism of ozonization. Deformation of vulcanizates, which increases their surface area, intensifies degradation, but reduces the effects of diffusion of ozone.

Ozone cracking occurs in three stages: viz., adsorption of ozone on the rubber surface, chemical reaction between ozone and the polymer (i.e., degradation) and mechanical growth of the cracks as a result of fatigue. The effect of the chemical stage, which is the most important in cracking, can be reduced by lowering the concentration of reactive sites (e.g., reducing the degree of unsaturation, introducing polar groups) or by addition of anti-oxidants. Depending on rubber type, the resistance to ozone cracking can be increased from 1.5-3 to 10 times by conventional rubber antioxidants in increased concentrations (5 to 10 phr). These compounds include amines, phenols, sulfur-containing compounds, aminophenols, and aromatic diamines. Their effectiveness can be increased by the addition of 1 to 2 phr of microcrystalline waxes. Highly reactive additives apparently react with ozone on the surface of the rubber before it can penetrate to the unsaturated bonds of the polymer. Hence, to be effective, an inhibitor must migrate to the rubber surface (and the surface of the cracks) at a high rate. Microcrystalline waxes presumably promote migration of inhibitors, protect them from oxidation by oxygen, and prevent their crystallization. A list of ozone cracking inhibitors produced commercially in the USSR and in other countries, including their applications to various types of rubbers, is appended.

PDL-41814

Zuev. Yu. S. and S.I. Pravednikova.

[THE INFLUENCE OF OZONE CONCENTRATION ON THE CRACKING OF RUBBER]
(in Russian).

Nauch.-Issledovatel.' Inst. Rezin. Prom. Trudy No. 6:3-15. 1960.

[Rubber, stress, ozone, cracking, mechanism]

The relation between ozone concentration and rubber cracking, and the effects of deformation on this relation were investigated. Experiments were carried out at various temperatures on SKS-30, a noncrystallizing, ozone-sensitive synthetic rubber, and on Nairit, a crystallizing synthetic rubber with relatively high ozone resistance. The ozone concentration range was 0.0002 to 0.15%; the deformation range was 6 to 150% for SKS-30, and 30 to 500% for Nairit. The method was based on the maintenance of a constant deformation by adjusting the load to the diminishing cross-sectional surface area of the sample. The cracking process was evaluated by determining t_0 , v_0 , and the time of rupture, t_1 . The relation between each of these characteristics and ozone concentration c , could be expressed: $\log t_0 = \log K_1 - n_1 \log c$; $\log v = \log K_2 + n_2 \log c$; and $\log t_1 = \log K_3 - n_3 \log c$, where K_1 , K_2 , and K_3 , and n_1 , n_2 , and n_3 are coefficients depending on the deformation of the sample. The tabulated values of these coefficients show that with increasing deformation, n_1 decreases slightly for SKS-30, and remains constant for Nairit, whereas K_1 increases for SKS-30 and decreases for Nairit. Values of n_2 and n_3 remain approximately constant for the deformation range tested, and are equal to 1.0 and 0.9 to 1.0,

respectively. K_2 goes through a maximum at the critical deformation. Consequently, the curves of v as a function of c are, at various deformations, parallel straight lines. A similar relation exists between t and c . The coefficient, n_3 increases rapidly with decreasing temperature (2.5 to 5.8 at -8 C). The general character of the dependence of t_0 , v , and t_1 on deformation and the critical deformation value remain essentially unchanged within the ozone concentration range used. Analysis of reaction kinetics shows that the average growth rate of cracks (v_p), in the absence of diffusion, is proportional to the rate of chemical degradation. If the concentration of ozone on the polymer surface is expressed by the Freundlich absorption equation, then $v_p = Ac^n$, where A and n are constants. This is in agreement with the relation between t_1 and c , determined experimentally. The increase of n_3 at low temperatures is explained by the effect of temperature on the chemical reaction rate. The role of diffusion in ozone cracking appears unimportant, at least for rubbers subjected to deformations.

The determination of ozone concentration at which rupture occurs within a given time at the critical deformation is a better criterion than rupture time at a given ozone concentration. Straight lines, representing $\log t_1$ as a function of $\log c$ for several rubbers at the critical deformation, are not parallel to each other. At constant rupture time, the order of increasing ozone resistance in which these rubbers can be arranged is different at low than at high ozone concentrations. For each rubber, the order in which samples, subjected to various degrees of deformation can be arranged, does not depend on the ozone concentration within the generally used range. However, at high ozone concentrations, the differences between t_1 values are considerably smaller than at low concentrations.

PDL-41937

Bevilacqua, E.M. and E.S. English.
THE SCISSION STEP IN HEVEA OXIDATION.
J. Polymer Sci. 49:495-505. 1961.

[Rubber, oxidation, mechanism]

PDL-42017

Pendle, T.D.
A NEW METHOD OF INCREASING THE FLAME RESISTANCE OF NATURAL RUBBER.
Rubber Developments 14(2):42-45. 1961.

[Rubber, fireproofing]

The flame resistance of natural rubber is increased by reacting rubber in the latex state with bromotrichloromethane (CBrCl_3). The reaction is preferably carried out below 30 C, and is initiated by a redox catalyst and stabilized by sodium dodecyl sulphate or potassium laurate. Because the four halogen atoms are attached to one double bond, the number of remaining double bonds remains high and the same vulcanizing processes can be used as for unmodified rubber.

The maximum modification possible results in a product containing about 74% by wt of CBrCl_3 (designated by FR 74); the greater the modification the greater the flame resistance. At 15% (FR 15 rubber), a vulcanized film is self-extinguishing in a flame test.

However, since tensile strength is decreased with increase in CBrCl_3 content (e.g., tensile strengths in kg/sq cm are 300, 185, 175, 120 for natural rubber, 12%, 15%, 20% CBrCl_3 respectively), 20% is the practical limit.

Addition of 5 to 10 parts by wt antimony trioxide to a FR latex improves flame resistance without sacrificing tensile properties. Such films are self-extinguishing if they contain 12% CBrCl_3 . Higher strengths may be obtained by a technique similar to masterbatching, in which a more highly modified (e.g., FR 30) latex is blended with natural latex to reduce the CBrCl_3 content to the required level (e.g., 12%) to give a blended product designated as FR 30/12. Tensile strengths in kg/sq cm are 185 for 12% CBrCl_3 , 220 for FR 20/12, and 235 for FR 30/12. At high blend rates there is a slight increase in tension set and a small decrease in flame resistance.

PDL-42048

Boucher, Madeleine and Jacqueline de Merlier.

UTILISATION DE LA LAMPE A XENON POUR LA REPRODUCTION DU
VIEILLISSEMENT A LA LUMIERE (Reproduction of Light Aging
Using the Xenon Lamp).

Rev. Gén. Caoutchouc 38:225-229. February 1961.

[Rubber, light, tests, lamp] .

Samples of fifteen rubber vulcanizates, differing in composition and in color, were subjected to natural aging by outdoor exposure in Paris at a 45° angle for 10 to 60 days and to accelerated aging by irradiation with a xenon lamp (Xenotest WL) for 25 to 140 hr at 35 C and 60% RH. The Xenotest lamp has a spectrum similar to that of sunlight. The initial colors of the samples ranged from pure white through ivory, beige, light brown and dark brown. Aging, determined by refractometry, intensified the original color of all samples. There was good correlation between color intensity after 25 and 140 hr accelerated aging and after 10 and 60 days of natural aging, respectively. Some of the rubbers subjected to natural aging (both rain and sunshine) assumed a pink coloration after about 30 days; rubbers subjected to accelerated aging did not. There was good correlation between the time of appearance of cracks and their development into a network in rubbers exposed to Xenotest for 50, 90, and 140 hr and samples exposed to outdoor conditions for 30, 50, and 60 days, respectively. A similar correlation was observed for loss of mechanical strength (resistance to rupture). The Xenotest apparatus is considered to be suitable for evaluating photochemical degradation of rubber vulcanizates.

PDL-42188

Dunn, J.R. and J. Scanlan.

CHANGES IN THE STRESS-STRAIN PROPERTIES OF NATURAL RUBBER
VULCANIZATES DURING AGEING.

Faraday Soc., Trans. 57:160-166. January 1961.

[Rubber, vulcanizate, aging, stress, mechanical properties, mechanism]

PDL-42429

Montermoso, J.C. and F.R. Fisher, eds.
PROCEEDINGS: SIXTH JOINT ARMY, NAVY, AIR FORCE CONFERENCE ON
ELASTOMER RESEARCH AND DEVELOPMENT. VOL. 1.
October 1960. 264 p.

[Symposium elastomers, polymers, polymers (inorganic), fluoro-carbons, polyethylene, polyesters, silicones, vinyls, lead compounds (organic), urethan, nitroso compounds, radiationproof, temperatureproof, synthesis, mechanical properties]

PDL-42444

Zuev, Yu. S. and S.I. Pravednikova.
METHODS OF TESTING THE RESISTANCE OF RUBBERS TO OZONE CRACKING
(in Russian).
Kauchuk i Rezina 20:30-32. January 1961.

[Elastomers, ozone, cracking, tests, foreign]

Standard methods for testing resistance of rubber products to ozone cracking involve the time of appearance of cracks (t_1), and the degree of cracking. The last characteristic is arbitrary and has no definite physical meaning. Sometimes it reflects the rate of crack growth. The time of appearance of cracks also is arbitrary, since it depends on the test conditions, but is quantitative. Another quantitative characteristic, the rupture time (t_r), which reflects the actual wear resistance of rubbers, is not included in the standard methods. According to available data, t_1 is 10% or less of t_r . Unlike t_1 , which decreases gradually with increasing deformation stress, t_r goes through a minimum, corresponding to a critical deformation. The test deformations, recommended in the standard methods (20, 16 and 25, and 50% stretching), for many rubbers include the critical deformation. Since this value depends on the composition of the rubber, in testing new products it is important to apply a wide range of deformations. At various deformation levels, the effects of additives such as fillers, waxes and antioxidants on the minimum t_r are different. Consequently, the deformation range applied in testing should correspond as closely as possible to the actual stress conditions to which a rubber product will be subjected. For uniform stress distribution, test samples should be rectangular strips. The relative resistance of rubbers depends on the concentration of ozone used in tests. The effects of antioxidants and their diffusion to the rubber surface also must be considered. At low ozone concentrations and prolonged test time this factor plays a more important role than at high ozone concentrations and short test time. Hence, tests should be carried out not at one but at several levels of ozone. The critical deformation does not depend on ozone concentration, but is affected by temperature. Consequently, the temperature range used in tests should be close to that at which the rubber will be used.

PDL-42515

Levi, Morton W.
HOW TO INHIBIT RUBBER DETERIORATION IN SWIM SUIT FABRICS.
Knitted Outerwear Times 30(30):24. July 1961.

[Rubber, swelling, water, dimensionproof, lubricants, clothing]

PDL-42576

Cheetham, I.C. and W.A. Gurney.
OZONE-AIR VELOCITY FACTOR IN OZONE-CRACKING.
Inst. Rubber Ind., Trans. 37:35-42. April 1961.

[Rubber, ozone, cracking, test]

The effect of airspeeds on ozone cracking of rubber was tested in small wind chambers with air velocity controllable up to 350 cm/sec under conditions of (1) varied ozone concentrations at constant ozone-air velocity, and (2) varied ozone-air velocities at constant ozone concentration. Ozone was produced by silent discharge and estimated by a KI-I₂ absorption train method. The extent of ozone attack was measured by rate of ozonometer deflection which is proportional to the rate of stress relaxation in a standard rubber thread specimen.

Results indicate that only at higher velocity is ozone attack commensurate with the true ozone concentration. At lower ozone-air velocities, the rate of cracking is critically dependent on air-speed; lowering the ozone-air velocity produces the same effect as lowering the ozone concentration. The degree of cracking with 200 pphm ozone at 50 cm/sec was similar to that with 100 pphm ozone at 350 cm/sec. These effects introduce the concept of an effective ozone concentration as differentiated from the true concentration. Mechanisms of the interactions are described. An appreciation of this relationship may help standardize the ozone testing procedure and aid correlation of interlaboratory test results.

PDL-42577

Buswell, A.G.
THE XENON LAMP: AN EVALUATION OF THE TENDENCY OF RUBBER COMPOUNDS TO DISCOLOUR ON EXPOSURE TO LIGHT AND OF PVC COLOURS TO FADE.
Inst. Rubber Ind., Trans. 37:43-51. April 1961.

[Rubber, poly(vinyl chloride), discoloration, oxidationproofers, amines, phenols, tests, light, accelerated, comparison]

A titanium dioxide loaded white rubber compound and a clay loaded natural rubber cable compound, each containing a wide range of phenolic and amine antioxidants, were tested for light discoloration outdoors in the open, outdoors under Perspex, as well as under a xenon lamp, a carbon arc, and a mercury discharge lamp.

Exposure tests in the open result in smaller differences in discoloration between phenolic and amine antioxidants when tested under standard Perspex containing an ultraviolet absorber. Weathering and chalking only occur in samples exposed in the open. Outdoor tests are not reproducible. Emission from the xenon lamp has a spectral distribution similar to natural sunshine in northern latitudes, whereas that of the carbon arc and mercury lamp is too

rich in ultraviolet. Xenon lamp results correlate reasonably well with outdoor tests under Perspex, and have good reproducibility. The carbon arc gives poor reproducibility; the mercury lamp gives reproducible results, but poor discrimination among compounds.

Fading tests were carried out on poly(vinyl chloride) containing five different types of pigments. A reasonably good correlation was found between the ratings obtained under outdoor exposures and with a xenon lamp, but not with a carbon arc or mercury lamp.

PDL-42613

Gagne, Joseph L.
METHOD OF MAKING NATURAL RUBBER RESISTANT TO OZONE BY THE ADDITION
OF POLYTETRAFLUORETHYLENE AND PRODUCT THEREOF.
U.S. Pat. 3,002,938; October 3, 1961. [2] p.

[Rubber, ozoneproofing, polytetrafluorethylene, patent]

Molded natural rubber is made resistant to ozone cracking by addition of 0.75 to 2.5% polytetrafluorethylene. The compound is added to the rubber mix just prior to adding sulfur and vulcanizing.

PDL-42631

Gleim, William K.T.
ANTIOZONATION OF RUBBER WITH SUBSTITUTED PHENOLS.
U.S. Pat. 2,984,694; May 16, 1961. [3] p.

[Rubber, ozoneproofing, chlorinated phenols, patent]

Ozone cracking of sulfur-vulcanizable rubber is prevented by addition of 0.25 to 10%, preferably 2 to 5% by wt of the rubber hydrocarbon, of a phenol having an alkoxy group with 1 to 6 carbons in the 2-position, an alkyl group of 1 to 6 carbons in the 4-position, and chlorine atoms in the 5, 5 and 6, or the 3, 5, 6 positions on the benzene ring. Claimed compounds are 2-methoxy-4-methyl-5,6-dichlorophenol and 2-methoxy-4-methyl-3,5,6-trichlorophenol.

PDL-42664

Natural Rubber Producers' Research Association, London (Maurice Woodall Philpott).
IMPROVEMENTS IN AND RELATING TO THE PRESERVATION OF NATURAL RUBBER.
Gt. Brit. Pat. Spec. 859,796; January 25, 1961. 7 l.

[Rubber, ageproofing, latex, patent]

Age resistance of unvulcanized natural rubber in dry or latex form is improved by addition of 0.005 to 5.0 pph of thiourea or a derivative in which a hydrogen on one or both of the amino groups is replaced by an alkyl, aryl, hydroxyalkyl or hydroxyaryl group. The inhibitors may be added at any desired stage.

PDL-43021

~~Bergstrom, E.W.~~

~~INDOOR AND OUTDOOR AGING OF ELASTOMERIC VULCANIZATES OVER A TEN
YEAR PERIOD.~~

U.S. Arsenal, Rock Island, Ill. Laboratory. Report 61-3868.
October 1961.

[Elastomers, aging, weathering, packaging, tests (protected)]

Based on changes in ultimate elongation and strain values on yearly inspections over a 10-yr period, chloroprene/isoprene, butadiene/acrylonitrile and isobutylene/isoprene vulcanizates aged more outdoors (Rock Island, Illinois) than indoors. Butadiene/styrene vulcanizates aged approximately the same amount in both locations. Isobutylene/isoprene vulcanizates aged least both indoors and outdoors. Low temperature stiffness properties of all vulcanizates remained virtually unchanged after 10 yr of indoor aging.

Wrapping of test pads in kraft paper, polyethylene and a vinyl coated aluminum foil/asphalt impregnated kraft paper laminate made no significant difference in the aging of any of the vulcanizates except those prepared from chloroprene/isoprene copolymer. These vulcanizates when wrapped in the foil-paper laminate retained their original physical properties better than unwrapped vulcanizates or those wrapped in the other two materials.

Some correlation was observed between the properties of vulcanizates aged in an air oven at 158 F and vulcanizates aged indoors and outdoors over the 10-yr period. However, oven aging was not sufficiently severe to be considered an accelerated test.

Five years of indoor or outdoor storage are considered to be the maximum for general purpose rubber such as used in this study. Special compounding or use of specialty elastomers may extend storage life.

PDL-43048

Schaefer, Charles.

A QUANTITATIVE OZONE TEST.

Rubber World 145:79-85. February 1962.

[Elastomers, ozone, cracking, tests]

Static ozone damage to elastomers is determined easily and quantitatively by a method based on the fact that crack volume is proportional to the extent of ozonation itself. Since increase in thickening during ozonation of a rubber specimen stretched to constant elongation is proportional to extent of ozone crack volume, it can be used to measure ozone damage with good reproducibility.

Tests with NBR and SBR stock with and without two commercial antioxidants showed that thickness of the rubber specimen is not related to ozone damage and that extent of damage is inversely related to test temperature in the range 90 to 130 F. A first order dependence on ozone concentration is indicated by a plot of crack volume against ozone concentration with time and temperature constant. Ozone damage is greatest at 20% elongation; decrease is initially rapid, and becomes increasingly slower with increasing elongation. Elongations less than 20% are not well adapted to this method, nor are changes occurring early in the experiment. The test does not permit observations of time to first crack.

PDL-43383

Minckler, Leon Sherwood, jr. and others.
RUBBER WITH A CYCLIC TRIENE THEREIN.
U.S. Pat. 3,005,805; October 24, 1961. [3] p.

[Elastomer, ozoneproof, patent]

Ozone resistance of various vulcanizates, particularly butyl rubber, is increased by addition of a cyclic triene; 1,5,9-cyclododecatriene is claimed. Addition of 5.0 phr of the triene raised ozone resistance of a butyl vulcanizate about 400% after exposure to 0.2% ozone at 50% elongation. Decreases in cure rate and physical properties by the cyclic triene may be counteracted by addition of more sulfur and Tuads accelerator to the formulation.

PDL-44679

Iyer, H.N. and P.K. Choudhury.
STUDIES IN NATURAL RUBBER. PART IV. DEPOLYMERISATION OF NATURAL RUBBER IN PRESENCE OF SUNLIGHT AND AIR.
Indian J. Appl. Chem. 24:133-139. 1961.

[Rubber, light, depolymerization]

South Indian Hevea crepe and smoked sheet were exposed to sunlight for various periods with periodic measurement of solution viscosity, solubility, and weight gain. Exposed crepe was sufficiently tacky within 2 days; after 4 to 5 days it was too tacky for handling. Intrinsic viscosity gradually fell to a constant value of 0.65 after 45 hr. Solubility in toluene first rose and then fell. Oxygen absorption rose from 0.055% at 3 hr to 2% at 72 hr. Smoked sheet became hard and inelastic initially; intrinsic viscosity increased. Tackiness developed after 12 to 13 days. After initial decrease, solubility rose. Crepe exposed 2 days was masticated in 6 min vs. 18 min for unexposed rubber. The two vulcanizates were comparable. Initial plasticization by sunlight is considered to be commercially practical.

PDL-45038

Zuev, Yu. S., S.I. Pravednikova, and G.V. Kotel'nikova.
[EFFECT OF FILLERS AND PLASTICIZERS ON THE RESISTANCE OF RUBBERS TO OZONE CRACKING AT VARIOUS DEFORMATIONS] (in Russian).
Kauchuk i Rezina 20(11):15-21. November 1961.

[Rubber, elastomers, ozone, cracking, carbon black, fillers, plasticizers, foreign]

The study included natural rubber (NK), SKB (butadiene polymer), SKS-30 (butadiene-styrene), SKN-40 (butadiene-acrylonitrile), and Nairit (chloroprene rubber) filled with carbon black (an active filler) and calcium carbonate (an inert filler). The effect of a plasticizer (dibutyl phthalate) was studied on NK, SKN-40, and Nairit. At each stress applied, the resistance to ozone cracking was evaluated by measurements of the rupture time, π_r , and the time of appearance of the cracks, π_i .

Both fillers reduced π_r and π_i ; the extent of reduction was related directly to their concentration. With increasing deformation,

π decreased steadily; π when through a minimum at the critical deformation Σ_{er} . Carbon black caused a marked shift of Σ_{er} toward higher deformations in NK and SKB. In the polar rubber SKN-40, the shift was less pronounced, and in Nairit it was practically absent. The inert filler had no effect on Σ_{er} .

Plasticizer caused reductions of π and π_r (more marked in SKN-40 and Nairit than in NK). It did not affect the Σ_{er} of NK, but shifted the Σ_{er} of the two other rubbers toward smaller deformations. Deformation vs. π_r curves of Nairit, subjected to the action of ozone and, simultaneously, to two-dimensional deformation, showed no minimum. This presents additional evidence for the effect of intermolecular forces on Σ_{er} . Two-dimensional deformations prevent, to a large extent, molecular orientation and, as a result, there is no critical deformation and no corresponding minimum rupture time. Active fillers, such as carbon black, increase intermolecular forces in nonpolar rubbers, but affect polar rubbers considerably less, and hence, cause a smaller shift of Σ_{er} . Inert fillers, which do not react with the polymers, have no effect on Σ_{er} . Dibutyl phthalate weakens the intermolecular forces and therefore shifts Σ_{er} in the opposite direction.

The more pronounced effect of fillers at high deformation on π_r is apparently related to an increased number of cracks appearing at low deformations in filler rubbers as compared with nonfilled rubbers, and to the resulting reduction of stresses in the cracks. At high deformations, when there is a large number of cracks in non-filled vulcanizates, the effect on internal stresses of additional cracks due to the filler is relatively small.

PDL-46043

Zuev, Yu. S. and V.F. Malofeevskaya.
EFFECT OF MOISTURE ON THE RESISTANCE OF RUBBER TO OZONE CRACKING.
Soviet Rubber Technol. 20(6):23-26. 1961.

[Rubber, elastomers, ozone, cracking, air, water vapor]

Ozone cracking of deformed rubbers occurs much more slowly in water than in air, even with similar molar concentrations of ozone. If, however, the surface of the rubber is made hydrophobic by the addition of paraffin wax there is a considerable decrease in the protective action of water. In moist air, water has a retarding effect only for those vulcanizates of a definitely hydrophilic nature (natural rubber, polychloroprene). It has no effect on vulcanizates of sodium-catalyzed polybutadiene, 70:30 butadiene-styrene, carboxylated butadiene-styrene, and 82:18, 74:26, and 60:40 copolymers of butadiene-acrylonitrile. Introduction of paraffin wax reduces the protective action of atmospheric moisture on the hydrophilic rubber just as it does in water. The retarding effect of moisture is physical and is due to its absorption on the surface of the rubber and consequent swelling of the surface layer, the latter occurring more rapidly in water than in water vapor. As a result of swelling, tensile stress is reduced and more evenly distributed, strength properties are improved and resistance to ozone cracking is increased.

PDL-47395
(cont.)

Swim suits and related beach wear made of elastomer threads must withstand a certain amount of actinic exposure plus mechanical stresses equivalent to ~50% stretching or elongation. In an attempt to develop an accelerated screening test for gaging the suitability of various rubber textiles as beach wear, several series of natural weathering tests at different localities were made and compared with a number of artificial exposure methods, using several Weather-Ometers and Xenotest chambers.

The Xenotest instrument furnished a more suitable source of radiative energy consistent with the effects of natural actinic degradation of rubber threads. For accelerated testing, two sets of 25 rubber threads each should be exposed in this instrument, together with a 'blue scale' reference standard (under ordinary window glass) until the standard has discolored to stage 7 of the blue scale. This period of time is roughly equivalent to 2 or 3 summer seasons of natural weather. Rubber threads able to withstand this test without significant destruction ($\leq 10\%$ of the exposed threads) appear suitable for swim suits and the like. Degradation of the threads is observed under a microscope.

PDL-47457

de Merlier, Jacqueline and Jean Le Bras.
INFLUENCE OF CHEMICAL MODIFICATIONS ON THE OXIDIZABILITY OF
NATURAL RUBBER.

Ind. Eng. Chem. Prod. Res. Develop. 2:22-26. March 1963.

[Rubber, chemutation, oxidationproofing]

The chemical modification of natural rubber by means of reagents that combine either by blocking the α -methylenic carbons (e.g., maleic anhydride) or by saturating the double bonds (e.g., saligenol) decreases its oxidizability. In both cases, this decrease is not proportional to the number of reactive sites blocked, and only a relatively small number of combined groups suffices to reduce the oxidation rate notably. There are major differences in the course of oxidation, according to the mode of combination of the reagents. Tests were carried out on modified rubbers containing varying proportions of these reagents and their oxidizabilities at 80 C were measured manometrically. For the same number of reagent molecules per 100 isoprene units: (1) the oxidation rate is reduced initially with saligenol, but increased with maleic anhydride; (2) after a few hours, oxidation of saligenol rubbers continues at a noticeable rate, while that of maleic rubbers decreases abruptly almost to cessation. It is possible in this way to improve the resistance of raw rubber, and possibly also raw maleic rubber, to oxidation and this may influence the behavior of vulcanizates.

PDL-47502

Dunlop Rubber Company Limited, London, England (Inventors:
Charles Edwin Kendall and Philip Stanley Smethem).

VULCANISATION OF NATURAL OR SYNTHETIC RUBBER.

Gt. Brit. Pat. Spec. 907,831; October 10, 1962. 16 l.

[Rubber, elastomers, ozoneproofing, patent, thiourea]

PDL-47502
(cont.)

Natural and synthetic rubbers are vulcanized and at the same time protected from ozone by addition of 1 to 5% sulfur and 0.5 to 5% (preferably 1 to 2%) by wt of rubber of a thiourea (not an acid salt) having ≤ 4 aliphatic hydrocarbon substituents, the remaining substitutions being hydrogen. Identical groups of substituents are preferred. Vulcanizing is carried out at 90 to 160 C (preferably 140 C). Curing is hastened by zinc oxide and stearic acid or any other high-molecular weight fatty acid; retarded by an aliphatic amine. The thiourea is only partially decomposed during vulcanization and functions as an antiozonant. In tests with natural rubber 1 phr of tetrabutyl-, tetramethyl-, tributyl- or di-n-hexylthiourea used with 3 phr of sulfur was as effective as mercaptobenzothiazole or thiocarbanilide.

PDL-47503

Natural Rubber Producers' Association, London, England
(David John Graham and Derek Henry Taysum)
IMPROVEMENTS IN OR RELATING TO THE PRESERVATION OF RUBBER LATEX.
Gt. Brit. Pat. Spec. 908,283; October 17, 1962. 6 l.

[Rubber, latex, bacteria, storageproof, toxic, patent]

Hevea latex and concentrates are preserved by adding $\geq 0.001\%$ by wt of a thiobisphenol as an emulsion or dispersion or as an alkali metal or ammonium salt. Particularly effective is 2,2'-thiobis(4,6-dichlorophenol); it is nontoxic and nondiscoloring. The compound is applied as a spray at the tapping cup or panel, or as an anticoagulant in the cup or at the field collecting station. Ammonia should be present in the latex in 0.1 to 0.7% concentration. A satisfactory latex concentrate contains 0.2% ammonia and 0.3% of the sodium salt of 2,2'-thiobis(4,6-dichlorophenol). Bacterial count was < 10 per ml after 3 days and after 6 mo storage. In latex with 0.2% ammonia only, the count was 1.2×10^5 after 3 days, and the latex was completely coagulated after 6 mo. With 0.7% ammonia only, bacterial count was 2.2×10^3 after 3 days and 10 after 6 mo.

PDL-47504

Imperial Chemical Industries Limited, London, England (Inventor: Richard James Fielden).
ALKYL SUBSTITUTED HETEROCYCLIC COMPOUNDS.
Gt. Brit. Pat. Spec. 904,415; August 29, 1962. 9 l.

[Polymers, rubber, elastomers, ozoneproof, patent]

Polymers and natural and synthetic rubbers are protected from ozone by incorporation before vulcanization of 0.25 to 5.0% by wt of the rubber or polymer of one or more alkyl-substituted piperidines. Preferred compounds have an aryl substituent on the nitrogen. Synthesis of 8 compounds is described. Claimed compounds are N-phenyl-2-propyl-3,5-diethylpiperidine and its reaction product with formaldehyde.

PDL-48082

Hamilton, W.F., M. Levine, and E. Simon.
ATMOSPHERIC IODINE ABATES SMOG OZONE.
Science 140:190-191. April 1963.

[Air, ozoneproofing, contaminants, iodine]

Traces of iodine in test samples of irradiated photochemical smog atmospheres reduce the ozone content. Eye and respiratory irritation are reduced qualitatively. In smog generated ozone the volumetric ratio of ozone removed to iodine added is ~ 7:1 and the reaction is 90% complete in 10 min. In darkness in purified air, ratio is 4.8:1 and reaction is only one tenth as fast. In purified air exposed to sunlight, reaction ratio is 5.1:1 and the rate is as rapid as in smog generated ozone. The greater effectiveness of iodine in smog is not understood. In sunlight, the presence of iodine in volumetric concentrations about one order of magnitude less than that of the hydrocarbon and nitrogen dioxide reactants effectively suppresses the generation, or reduces the concentration, of either natural or artificial smog-formed ozone.

PDL-48425

Textile Research Institute, Princeton, N.J.
THERMAL CHARACTERISTICS OF COATED TEXTILE FABRICS, by Robert F. Schwenker, jr., Robert K. Zuccarello, and Louis R. Beck, jr.
U.S. Naval Supply Research and Development Facility, Brooklyn, N.Y.
Clothing and Textile Division. Contract N140(138)67979B,
Summary Report II, Progress Report 7 and 8. March 1963.

[Cotton, nylon, coatings (organic), elastomers, butyl, Hypalon, neoprene, pyrolysis, decomposition products, test equipment]

Apparatus devised for thermogravimetric analysis (TGA) is described; the device automatically records change in sample weight as a function of time and temperature. Effects of double coatings of butyl rubber, Neoprene W, and Hypalon 20 on cotton and nylon fabrics were studied; curves, including those for individual components, were obtained in air and in nitrogen at temperatures ≤ 500 C.

TGA data correlated well with earlier differential thermal analysis data. Butyl rubber coated systems were the most thermally stable; neoprene coated fabrics, the least. The most pronounced chemical interaction occurred between neoprene and the two textiles; there was some reaction with the butyl rubber coatings and less with Hypalon 20. The interaction mechanisms were largely nonoxidative.

Thermal degradation of cotton, nylon, butyl rubber and butyl rubber coated cotton was studied by gas chromatography. A pyrolysis technique is described whereby textile materials are degraded in the carrier gas stream of the gas chromatograph; degradation occurs in < 10 sec, and the products are analyzed immediately without precondensation. Thermal decomposition of cotton yielded ≥ 37 compounds; 20 were identified. The major products were always the same, regardless of the atmosphere. Nylon yielded ≥ 25 products. Decomposition data on butyl rubber and rubber coated cotton are also presented.

PDL-48440

Holbrow, G.L.

ATMOSPHERIC POLLUTION: ITS MEASUREMENT AND SOME EFFECTS ON PAINT.
Oil and Colour Chemists' Assoc., J. 45:701-718. October 1962.

[Air, contaminants, location, season, tests, analysis, coatings
(organic)]

The nature of atmospheric pollution and various standard methods of measuring it are described. Records of atmospheric sulfur dioxide and rain-water analysis data from two paint exposure sites in England, suburban and industrial, indicate the nature and concentration of pollution that is likely to affect paint films. Specific effects of pollution on paint are attack on young films by sulfur dioxide, causing delay in drying, production of water sensitivity, and possible attack on certain pigments; formation of crystalline bloom; and staining.

PDL-48445

Gould, R.D. and J.W. Linnett.

ELECTRONIC STRUCTURE OF OZONE.

Faraday Soc., Trans. 59:1001-1018. May 1963.

[Ozone, structure (molecular)]

PDL-48448

Izuchi, M. and others.

ON THE CORONA RESISTANCE PROPERTIES OF PLASTIC AND RUBBER MATERIALS (in Japanese with English summary).

Sumitomo Denki No. 79:70-74. November 1962.

[Polymers, elastomers, electric insulation, corona, tests, foreign]

Methods are lacking for testing synthetic rubbers and plastics used for high voltage insulation for corona deterioration; the breakdown mechanism of corona discharge is not thoroughly understood. Tests by needle-plane corona discharge of various cable insulants are described. Effects of changing the voltage, frequency, shape of the electrode, air gap distance, mechanical stress, and humidity are discussed.

PDL-48627

Morkel, Karl.

UBER BUTYLISOLIERUNG FÜR STARKSTROMKABEL UND -LEITUNGEN UNTER
BESONDERER BERÜCKSICHTIGUNG DER ALTERUNGSEIGENSCHAFTEN (Butyl
Insulation for Power Cables and Insulated Wires With Special
Reference to Aging Characteristics) (English summary).

Siemens Z. 36:664-669. September 1962.

[Butyl, electrical insulation, cable, wire, high temperature, service
life, foreign]

PDL-48660

Lyubchanskaya, L.I., L.S. Feldshtein, and A.S. Kuzminskii.

AGEING OF RUBBERS IN THE STRESSED STATE.

Soviet Rubber Technol. 21(1):20-25. January 1962.

PDL-48690

U.S. Office of Technical Services.

OZONE.

Selective Bibliography 509. September 1962.

[Ozone, ozoneproofing, rubber, elastomers, tests, air, analysis, bibliography]

PDL-48758

Salomon, G. and F. van Bloois.

THE MECHANISM OF OZONE CRACKING. I. OZONE CRACKING OF PLASTIC FILMS.

J. Applied Polymer Sci. 7:1117-1132. May 1963.

[Rubber hydrochloride, polymers, films, cracking, ozone, mechanism]

Stretched films from partly unsaturated natural rubber hydrochloride (Pliofilm of 3 grades) develop cracks and fracture in ozonized oxygen. Cracking occurs only above a stress level of $\sim 70 \text{ kg/cm}^2$. Ozone sensitivity increases exponentially with stress, but goes through a maximum near the yield point of the thermoplastic films. Unlike rubbers, which are much more unsaturated, these high-modulus materials do not undergo over-all stress relaxation prior to fracture induced by ozone. The rate of surface ozonization of an unstretched film, estimated gravimetrically and volumetrically, is similar to that of rubber surfaces. Physical and chemical changes of the ozonized surface are reported. Results are briefly compared with ozone attack on other nonrubber materials.

PDL-48759

Andrews, E.H. and M. Braden.

THE SURFACE REACTION OF OZONE WITH CHEMICALLY PROTECTED RUBBER.

J. Applied Polymer Sci. 7:1003-1013. May 1963.

[Rubber, ozoneproofing, mechanism]

Replica electron microscopy was used to elucidate the physical mechanisms by which various additives afford ozone resistance to natural rubber. Two classes of chemical antiozonants exist, namely, those that enhance the critical energy required for ozone cracking and those that retard the rate of crack growth. In this investigation N,N'-di-3-(methylheptyl)-p-phenylenediamine was used as representative of the first class and oleic acid as representative of the second. The first of these protective mechanisms involves formation at the exposed surface of an inextensible layer $\sim 100 \text{ \AA}$ thick and inert to further ozone attack. The process giving rise to rate retardation also involves the formation of a surface layer, but the layer is susceptible to further ozonolysis and, eventually, complete degradation.

PDL-49023

Park, J.D. and J.R. Lacher.

RUBBER RESEARCH: THE SYNTHESIS OF SPECIAL FLUORINE-CONTAINING MONOMERS.

U.S. Quartermaster Corps. Contract DA-19-129-QM-1926, Progress Report, Quarterly Report 7. July 1963.

- PDL-49076 Himmel, L., J.J. Harwood, and W.J. Harris, jr., eds.
PERSPECTIVES IN MATERIALS RESEARCH.
U.S. Office of Naval Research, ACR-61. Washington, U.S.
Government Printing Office. February 1963. 771 p.
- PDL-49088 Little, R.W.
ANALYTICAL DESIGN FOR ENVIRONMENTAL CONDITIONS.
Research and Develop. 14(7):48-49. July 1963.
- PDL-49310 Thomson, G., ed.
RECENT ADVANCES IN CONSERVATION. CONTRIBUTIONS TO THE IIC ROME
CONFERENCE, 1961.
London, Butterworths. 1963. 224 p.
- PDL-49418 Mayo, Frank R. and others.
ACCELERATED DETERIORATION OF ELASTOMERS.
Stanford Research Institute, Menlo Park, Calif. Project PMU-4204;
Contract DA-18-108-CML-7216-[A], 4th Quarterly Progress Report.
July 1963.
- PDL-49424 Thiokol Chemical Corporation, Trenton, N.J. Chemical Operations.
NITROSO RUBBER. RESEARCH, DEVELOPMENT AND PRODUCTION, by
Marvin M. Fein.
Report Trenton RD-343-Q1; Reaction Motors Division, Denville, N.J.
Report RMD 8576-Q1; Contract DA-19-129-AMC-69(X)O.I.9044. [n.d.]
- PDL-49427 Kössler, I. and V. Novobilský.
ULTRASONIC DEGRADATION OF POLYCHLOROPRENE AGED IN AIR.
Collection Czechoslov. Chem. Commun. 28:578-584. March 1963.

[Chloroprene, decomposition, aging, high temperature, sound,
mechanism]

Polychloroprene (Svitpren K) was aged in air at 80 C and the aged samples were fractionated. Ultrasonic degradation was determined with a fresh sample and fractions of the aged samples. Benzene solutions of the polymer in 0.3 to 0.6% concentration were examined in the presence of various gases.

Evidence obtained from the limiting degree of polymerization observed during ultrasonic irradiation and from the degradation rates of fractionated and unfractionated specimens showed that cross-linking occurred through the formation of labile peroxidic bonds which prevail in the first stage of aging. Infrared spectroscopy indicated an increased content of carbonyl groups in the first fraction. The number of bonds broken per unit time during ultrasonic degradation decreased with increased concentration of the polymer in solution. Of various gases, degradation decreased in the order air, nitrogen, oxygen and carbon dioxide.

PDL-49528 Levitin, I.A. and others.
[INVESTIGATION OF PHYSICAL ANTIOXONANTS OF DIFFERENT ORIGIN]
(in Russian).
Kauchuk i Rezina 22(4):14-17. April 1963.

PDL-49608 Boucher, M. and J. de Merlier.
SUR LA PROTECTION DU CAOUTCHOUC VULCANISÉ CONTRE LA DÉGRADATION
PROVOQUÉE PAR LA LUMIÈRE: ACTION DES ABSORBEURS D'ULTRA-VIOLET
(On the Protection of Vulcanised Rubber Against Degradation by
Light: Ultra-Violet Absorbers Action).
Rev. Gen. Caoutchouc 40:429-438. March 1963.

PDL-49622 Hurst, H.
SOME FURTHER DEVELOPMENTS IN THE USE OF LATEX-SILICONATE
COMPOSITIONS FOR DAMP-PROOFING MASONRY.
Rubber Developments 16:34-41. 1963.

[Rubber, latex, silicone, waterproofer, cement, masonry, plaster]

When a mixture of rubber latex and sodium methyl siliconate is applied to porous masonry, absorption is followed by a joint blocking effect of the pores which is not shown by the separate components. Development of water repellency by siliconate-treated pores involves neutralization of the siliconate by absorption of atmospheric carbon dioxide which results in condensation or polymerization of the siliconate into a silicone resin on pore surfaces. Rubber particles by their aggregation and coalescence cause physical blockage of pores; their adhesion to walls increases as walls become increasingly hydrophobic. The latex-siliconate may be applied on the surface by injection or by combined methods. The latex helps to prevent excessive diffusion of the liquid from the desired area of treatment. When it is injected, it arrests the vertical capillary spread of ground moisture and dissolved salts. Use of the multiple injection method for dampproofing of thick walls, cavity walls, irregular brick or stone walls, and random rubble filled walls are described. The injection method can also be used to prevent direct penetration of ground moisture as in basements or semibasements. Concrete screeds and renderings containing latex-siliconate have been satisfactory for years. Heat curing may extend the usefulness of the application to many specialized fields of concrete practice. Latex-siliconate can be used as a waterproofing additive for gypsum plaster to prevent direct entry of damp.

PDL-49630 National Research Council. Prevention of Deterioration Center.
PRESERVATION OF INACTIVE EQUIPMENT AND LONG-TERM STORAGE OF
MATERIALS, compiled by Hans Janecka.
PDC Search No. 63-045. November 1963.

PDL-49641 Peterson, Charles H.
RUBBER-METAL BOND FAILURES.
Rubber Age (N.Y.) 93:929-932. September 1963.

PDL-49723

Goodyear Aircraft Corporation, Akron, Ohio.
NEW AND IMPROVED MATERIALS FOR EXPANDABLE STRUCTURES. (PHASE II -
FILM AND ELASTOMER PERMEABILITY), by D.M. Marco, W.B. Cross,
and C.E. Welling.
U.S. Dept. of the Air Force. Aeronautical Systems Division,
Wright-Patterson Air Force Base, Ohio. Technical Documentary
Report 62-542, Part III; Contract AF33(616)-7854. April 1963.

[Radiation (electromagnetic), ultraviolet, vacuum, polymers,
elastomers, fluorocarbons, silicones, butyl, films, gas, perme-
ability, optics, transmission, mechanical properties, degradation,
mechanisms]

Polymeric films and certain elastomers for possible use in space
were evaluated for resistance to ultraviolet light in vacuum.
Effect on gas permeability was the principal factor investigated.
A semiempirical equation for predicting performance of an unirradi-
ated cloth-elastomeric combination prior to construction of the
fabric was examined.

Five commercially produced fluorocarbon films were very stable
to ultraviolet in vacuum; specimens that received total radiation
of 45,000 joules/cm² (~45 solar days) showed little change.
Infrared examination showed no structural changes; changes in
solution properties and in mechanical properties were small. The
most significant effect was in light transmission properties. All
fluorocarbons became more light absorbent with increased exposure;
increase was less in films containing little or no hydrogen (e.g.,
Alcllar 33c, Kel F-82, Teflon FEP). Significant changes in gas
permeability (helium) occurred only in Kel F-82 which increased in
crystallinity as a result of heating during irradiation.

Elastomers generally crosslinked as a result of ultraviolet
irradiation in vacuum. Silicone and butyl rubber show deteriorated
mechanical properties resulting from surface cracking; butyl suffered
chain scission in hot-spot areas. Viton A, a fluoroelastomer, did
not develop surface flaws; crosslinking effected a net improvement in
mechanical properties. Crosslinking of elastomers tended to reduce
gas permeability. The empirical equation investigated will predict
the permeability of a single- or multi-ply elastomer-coated
composite fabric.

PDL-49729

Ossefort, Z.T. and F.B. Testroet.
THERMAL-OXIDATION INHIBITORS FOR DIENE ELASTOMERS.
Rubber Age (N.Y.) 23:266-272. May 1963.

PDL-49781

U.S. Naval Shipyard, Brooklyn, N.Y. Naval Applied Science
Laboratory.
REPORT OF INSPECTION OF NEOPRENE COATINGS APPLIED TO HYDROFOIL
ASSEMBLIES OF HYDROFOIL CRAFT, HIGH POINT (PC(H)-1).
Lab. Project 9300-17, Technical Memorandum 1. September 1963.

PDL-49799

MOTHBALLING VEHICLES FOR OUTDOOR STORAGE.
S.A.E. J. 71(9):74-77. September 1963.

PDL-49866

Wardle, D.I., C.D. Walshaw, and T.W. Wormell.
A NEW INSTRUMENT FOR ATMOSPHERIC OZONE.
Nature 199:1177-1178. September 1963.

NATIONAL ACADEMY OF SCIENCES NATIONAL RESEARCH COUNCIL

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