TECHNICAL INTELLIGENCE
AMC

The U.S. GOVERNMENT

IS ABSOLVED

FROM ANY LITIGATION WHICH MAY ENSUE FROM THE CONTRACTORS INFRINGING ON THE FOREIGN PATENT RIGHTS WHICH MAY BE INVOLVED.

HEADQUARTERS

WRIGHT FIELD, DAYTON, OHIO

REEL — C

1344

A.T.I.

31601

303.12.

CONFIDENTIAL

8.2-20

Division 11

NATIONAL DEFENSE RESEARCH COMMITTEE

of the

OFFICE OF SCIENTIFIC RESEARCH AND DEVELOPMENT

OSRD No. 3506

Copy No. 44

CONFIDENTIAL

CONFIDENTIAL

Division 11
NATIONAL DEFENSE RESEARCH COMMITTEE
of the
OFFICE OF SCIENTIFIC RESEARCH AND DEVELOPMENT

FLAME THROWER FUELS

by
R. D. Dawson and E. R. White, Chemists
Shell Development Company

Report OSRD No. 3506
Copy No. 44
Date: April 20, 1944

Copy Nos.	
1-28	Dr. Irvin Stewart
29	Commandant, U. S. Marine Corps Headquarters Attention: Lt. Col. L. E. Marie
30	Office of the Chief of Chemical Warfare Service Attention: Technical Division, Liaison Branch
31-34	Chemical Warfare Center, Edgewood Arsenal Attention: Brig. Gen. W. C. Kabrich
35	Mr. E. P. Stevenson
36	Division 11 Files

Total Number of Copies - 45

This document contains information affecting the national defense of the United States within the meaning of the Espionage Act, U.S.C. 50; 31 and 32. Its transmission or the revelation of its contents in any manner to an unauthorized person is prohibited by law.

CONFIDENTIAL

CONFIDENTIAL

OSRD No. 3506

Division 11
NATIONAL DEFENSE RESEARCH COMMITTEE
of the
OFFICE OF SCIENTIFIC RESEARCH AND DEVELOPMENT
Section 11.3

FLAME THROWER FUELS

Service Directive: CWS-10

Endorsement (1) From E. P. Stevenson, Chief, Division 11 to Dr. Irvin Stewart, Executive Secretary of the National Defense Research Committee.

Forwarding report and noting:

> "This report covers a variety of studies on flame thrower fuels of the Napalm-gasoline gel type with particular emphasis on oxidation and oxidation inhibitors, and theories of gel structure."

This is a Final Report under Contract 11-394, OEMsr-916 with Shell Development Company.

CONFIDENTIAL

TABLE OF CONTENTS

CONFIDENTIAL

SUMMARY

The investigation covers various methods of obtaining thickened fuels for use in Flame Throwers, the purpose of this thickening being to provide a fuel having a high calorific value, ready ignitability, adhesiveness, resistance to disintegration in flight, and stability in storage.

In Section II of the report, tests on thickened fuels obtained by the following methods, 1) suspensions of small particles of combustible solids in the fuel base 2) emulsions of gasoline with various liquids and 3) gasoline gels are discussed. The bulk of the work was done on the last named, particularly on gasoline gelled with aluminum soaps. Certain other methods, however, might well repay further investigation.

Section III deals with possible variations in the Napalm (aluminum soaps of coconut, naphthenic and oleic acids) formula, the effect of water and free acid and soap complexity on gasoline gels. It is concluded that soaps made from cheaper and more readily obtainable sources of acid, e.g., Tall Oil, could probably be substituted for the standard Napalm acids.

The theory of gel structure is next discussed at some length, (see Section IV) particularly with regard to the effect of the addition of certain polar compounds, which are effective in preventing the oxidation of the Napalm soaps, both in the process of manufacture and in subsequent storage. It is concluded that a number of these oxidation inhibitors (UOP No. 5, Lorene, Alphatol, and Alphanil) can be used in sufficient concentration to prevent oxidation without danger of any deleterious effects on the gels prepared from these inhibited soaps.

In Sections V and VI the whole question of oxidation stability of Napalm is examined, an accelerated method for testing oxidation susceptibility described and the use of various oxidation inhibitors discussed. It is demonstrated that when unsaturated fatty acids are employed in the soaps used for gelation, the addition of these inhibitors facilitates manufacturing operations (particularly the drying process) and also insures against subsequent deterioration by oxidation on long storage, even under tropical conditions. They will also function beneficially in overcoming the deleterious effects of iron although, in the interests of economy, the iron content should be held to a minimum.

Experimental work on various methods of determining the moisture content of aluminum soaps is described in Section VIII. No definite recommendation can be made as to the method to be adopted because, although each method gives results that are reproducible, for a given sample of soap the water content varies according to the method used.

In Section IX the use of various additives to eliminate unburnt residue, increase density, etc., is discussed. Here again, no very definite

CONFIDENTIAL

FIDENTIAL

Page 2 of Summary.

recommendations can be made as sufficient data were not obtained. The best results were observed with a mixture of two parts aluminum dust, sixteen parts potassium perchlorate, and one hundred parts gel (8% Napalm in gasoline). This burns completely to an ash, the burning period is extended, and the total number of calories produced is increased.

In conclusion, additional lines of research which might repay further investigation are briefly indicated.

I. **Introduction.** The purpose of the investigation, the results of which are embodied in the present report, was to develop a suitable thickened fuel for use in flame throwers. The main requisites of such a fuel are high calorific value and ignitability, stability in storage, adhesiveness, and resistance to break up in flight, thus permitting maximum range to be obtained.

When the above contract was entered into, this problem of producing a thickened fuel was presented without limitations as to the manner in which its solution was to be accomplished. Previous work had been done by other contractors, particularly on Aluminum Soaps (Napalm) and methacrylate resins with the result that certain obvious disadvantages of both these types of gasoline thickeners had come to light. Attempts, therefore, were made to find a thickening agent free from the drawbacks inherent in the aforementioned materials. In general, there appeared to be four possible methods of attack which are outlined below:

(a) Lowering the fluidity of the liquid fuel and at the same time retaining the properties of a Newtonian fluid either by cooling or by addition of a solute. This method, however, would result in the simultaneous reduction of both the escaping tendency and the inflammability of the liquid. It would not, therefore, appear to merit further consideration.

(b) Production of a semi-rigid, plastic structure in a liquid by the addition of mildly lyophylic particles of nearly colloidal size. As examples of this class of thickened fluid, drilling muds, oildag and non-hydrated starch pastes may be cited. The flow properties of this type vary from thixotropic to dilatant, and in general, their adhesiveness tends to be low.

(c) Emulsifying the fuel with gas or liquid. Ruling out foams, such emulsified fuels would offer the advantage of complete combustibility, assuming that two combustible liquids are used in making up the emulsion. One great disadvantage, however, of this type of fluid would be the need for adequate emulsifying equipment as well as filling apparatus at the forward base.

(d) Producing a semi-rigid gel structure in the fuel by addition of some extremely lyophylic material. The thickeners now in use such as Napalm belong, of course, to this latter class.

II. **Preliminary Laboratory Work.** Preliminary tests were made on the preparation of thickened fuels belonging to the last three of the above categories without, however, obtaining any outstandingly original results. These tests will now be recorded, however, mainly in order to prevent duplication, but at the same time they may possibly prove useful as indications for further research along somewhat similar lines.

(1) <u>Suspensions of small particles</u>. This class produces its thickening action by increasing internal friction and the properties of such suspensions may be briefly outlined at this point. *

Assuming approximately spherical particles, at about 48 per cent of solid, the suspension will have no mobility, regardless of particle size, as this corresponds to close packing of the spheres. As the suspension is diluted there is a region of plasticity or resistance to flow which may extend over a wide or narrow range of dilution, depending on the nature of the particles and their size. As the particle size decreases, the plasticity range of concentration becomes broader but at nearly colloidal size the mobility again increases owing to the interference of Brownian movement. With particles which adsorb the solvent and are sufficiently finely divided, the solvent layer adsorbed represents a considerable fraction of the immobile cross section when the particles rest on each other and, hence, a plastic solid is produced with less suspended matter than with unsolvated particles. Thus, a sample of "colloidal" graphite which was both finely divided and solvated was plastic at a concentration of 5.6 per cent, whereas a coarser sample of clay did not resist deformation until a concentration of 20 per cent had been exceeded.

As it is desirable to have a thickening agent which will not reduce the calorific value of the fuel to a marked extent, tests were made using combustible powders. Lampblack and graphite, it was found, could not be dispersed in gasoline without settling, even if passed through a colloid mill. The addition, however, of 0.5 per cent of Napalm to the fuel acted as a peptizing agent and resulted in the carbon being dispersed during one passage through a suitable colloid mill. Dispersions obtained in this manner were almost as fluid as the gasoline itself when 15 per cent of carbon had been added but, on flocculation with a small amount of acetic acid, became quite thick and did not settle over a period of a month. These suspensions were thixotropic and possessed only a slight degree of elasticity.

The above lampblack suspension was projected, unignited, from the only device on hand at the time, namely, a gun made by conversion of a single cylinder motor, the gas explosion in the cylinder being used as a source of propellant energy. As a result of the violent pulsating agitation of the fuel produced by this device, the suspension was about 90 per cent

---

* For more complete discussion see Bingham, "Fluidity and Plasticity", McGraw-Hill.

atomized at the nozzle. A few small pieces traveled the same distance as a Napalm gel propelled by the same means but the trials were, on the whole, unsatisfactory and were not repeated when a more effective propelling device became available as, in the meantime it had been found by static burning tests that nearly all the carbon remained as an unburned residue, which shrank and peeled off the target as the gasoline burned away.

Formation of a suspension of sulfur in gasoline was then attempted by simultaneously passing hydrogen sulfide and sulfur dioxide through the liquid. The reaction was slow until the gasoline became saturated with sulfur and water, whereupon the sulfur then precipitated as a crystalline curd. Owing to the appreciable solubility of sulfur in gasoline any small particles formed soon dissolved and reprecipitated in macrocrystalline form so that no permanent suspension was obtainable.

Red phosphorus, finely ground, required the addition of a little Napalm in order to peptize it in gasoline, but when the fuel was burned it was found that the soap layer on the residue prevented combustion, the net result being the same as with carbon.

In conclusion, the fuels belonging to this category do not appear to be promising, mainly as a result of their low cohesive strength. However, a combination of this class with the gelling agents is later taken up under the heading of Loaded Fuels.

(2) <u>Emulsions</u>. If a stiff elastic emulsion of gasoline in an immiscible, inflammable liquid could be produced, a completely burnable fuel would result. In order to produce such an emulsion with a relatively small quantity of additive, the latter must form the outer phase and, in order to increase the permanence of the emulsion, a stabilizer should also be added. Moreover, to cause adherence to the target, the outer phase should both wet the latter and, at the same time, be viscous enough to prevent slippage.

On cursory inspection the indications are that ethylene glycol or the lower glyceryl ethers, carbitols and cellosolves would appear to satisfy the requirements fairly well. An experiment using 5 per cent glycol, 0.5 per cent ordinary soap and 94.5 per cent gasoline failed as the low surface activity of the soap in glycol solution prevented the formation of a sufficiently stable emulsion. This line of approach was not pursued further owing to the assignment of the main problem, but it is one that might very well repay further investigation.

(3) Gels. Of the ashless compounds, the following materials were tried, but in no case were satisfactory results obtained.

Pyroxylin dissolved in ethyl acetate, acetone or as collodion is lyophobic when added to gasoline, either a gelatinous precipitate or an easily synerizing gel resulting. The precipitate packs on pressing and is, therefore, unsuitable.

Cellulose acetate precipitates when an ethyl acetate solution is added to gasoline.

Polyisobutylene, M.W. = 100,000, slowly dissolves in gasoline but too much, about 15 per cent, is required to thicken the latter, the resultant product being sticky.

Polystyrene, a hard sample of unknown molecular weight, dissolved in benzene-acetone but precipitated on adding gasoline.

Polyallyl linoleate showed slight swelling in gasoline. Despite the foregoing failures, it is possible that, under different conditions, some of the above compounds might have given more satisfactory results.

The results on several soap type additives are tabulated below. The terms oleate, stearate, etc., are applied to the technical products though their actual composition is usually far from that which the name would indicate. Merck's "stearic acid", for example, contains from 30 to 50 per cent stearic acid, and 50 per cent pure oleic acid is an exceptional occurrence in the technical red oils or oleic acid U.S.P.

Action of Gasoline on Various Soaps
(5% Soap - 95% Gasoline - Room Temperature)

Soap	Action
Aluminum Oleate	Minor swelling - considerable $Al(OH)_3$ present.
Aluminum Resinate	None
Aluminum Stearate	None
Magnesium Stearate	None
Lead Linoleate	Partly soluble, leaving precipitate
Lead Oleate	None
Zinc Stearate	Very slight swelling - lyophylic
Zinc Palmitate	Solvates and becomes thixotropic
Zinc Resinate	None
Calcium Stearate	None
Trimethyl Benzyl Ammonium Stearate or Oleate	Little swelling
Lithium Stearate	None

Aluminum, magnesium, calcium and zinc ions tend to form co-ordination compounds with organic substances containing oxygen or nitrogen. These addition complexes are usually more oil soluble than the unco-ordinated salts. As nitrogen is particularly effective in this respect, trials were made with some of the above compounds to ascertain the effect of such co-ordination. The nitrogen bases chosen were quite weak as to basic strength in order to prevent metathesis with the metal soaps. Picoline, pyridine and two cuts of petroleum nitrogen bases were tried. All gave similar results but slightly greater effects were produced by the petroleum bases.

Action of Gasoline on Metal Soaps Peptized by Petroleum Nitrogen Bases.
(8% Soap - 92% gasoline - 2 mols of base per mol of soap)

Soap	Action
Zinc Palmitate or Stearate	Swells to a gel which is thick but not very cohesive
Calcium Stearate	Swells but is inferior to zinc salts in thickening power
Magnesium Stearate	Dissolves above 35°C, sets to a tender gel below 35°C
Aluminum Stearate	Dissolves completely, sets to a gel at -25°C
Lead Oleate	None

Comparison of the data in the above two tables gives some idea of the relative tendency of these ions to co-ordinate and suggests that the same type of change may be responsible for the disastrous effect of water on Napalm gels.

III. Possible Variations of the Napalm Formula. The next phase of the problem to be taken up was the possibility of modifying the existing Napalm formula. This type of gelling agent, which had already been extensively investigated by other workers in the field, consists of a mixture of the aluminum soaps of coconut, oleic and naphthenic acids. It seemed desirable to substitute, if possible, cheaper and more readily available materials for the naphthenic and coconut acids, especially since these materials for the most part have to be imported. Moreover, if at the same time a satisfactory soap or mixture of soaps could be made from acids of higher equivalent weight, less aluminum salt per pound yield and, also, less of this aluminum soap would be required to produce a gel of given viscosity. A cursory investigation of several native acid sources was, therefore, carried out, the materials tried being the acids derived from crude cottonseed, sardine and tall oil. When soaps were prepared from these acids according to the usual procedure using 3 mols of caustic, 2 mols of acids and a mol of aluminum sulfate, it was found that their gelling properties differed considerably from the normal Napalm soaps. Thus, with a given water content, the soaps in question gave stiffer, shorter gels and, moreover, the time of gelation increased considerably as compared with Napalm gels. However, by increasing the amounts of water and free acid in these soaps, products could be obtained which would duplicate Napalm in producing a specification gel. These observations were made by comparing a supposedly specification Napalm with the samples mentioned by means of a falling ball arrangement, since no Gardiner mobilometer was available at the time. It was, therefore, apparent that there was nothing unique about the Napalm formula and that by proper control of the composition of the product, acids derived from other sources could very well be used.

At the same time it was noted that, if uncombined polar compounds such as water, free acids and phenols were removed from commercial Napalm by extraction with acetone, a product resulted which was similar to the soaps from tall oil, etc., in that it set slowly to give short gels and, if the extraction were complete enough, residues were produced which would not swell in gasoline.

As the foregoing effects required some explanation and a more quantitative substantiation, a Napalm soap was made by precipitating a neutral soda soap mixture with basic aluminum sulfate. On extraction of this material with cold acetone to relatively constant weight, 13.2 per cent of extract was obtained which contained about 7 per cent of the soap weight of carboxylic acids, 2.1 per cent alkyl phenols, 3 per cent neutral oil and 1.1 per cent water. The fact that the latter came solely from the soap was not proved. The water content of the extracted soap was 0.3 per cent by the Dean and Stark method (4 hours extraction) and 1.2 per cent by the modified Fischer method (see section on water determination), while the unextracted material contained 1.1 per cent water Dean and Stark and 2.8 per cent by the Fischer method. The free acids were presumed to be approximately 0 and 7 per cent, respectively, on the two samples. It was later found that in non-anhydrous media, free acid could be extracted continuously at a slackening rate until a mono carboxylate was left as a residue. Therefore, the free acid content of the extracted soap was probably not zero when the measurements were made.* To the extracted sample, varying amounts of water and free Z-104-B (Napalm) mixed acids were added back and 8 per cent gels in Shell Premium gasoline were made up in Nessler tubes containing 1/2 inch steel balls. The rate of fall of the balls is given in the following table.

---

* See also McBain and McClatchie; J.A.C.S., 58 3266 (1932)

CONFIDENTIAL

Effect of Water and Free Acid on Gel Viscosity

Sample	% Added Water	% Added Napalm Acids	10 cm. fall time (minutes) of 1/2" Steel Ball	
			24 hours	48 hours
Napalm	0	0	515	45.8
Extracted Napalm	0	0	ca 6000	5000
	0.18	0	ca 5000	590
	0.55	0	2350	71.6
	0.84	0	3700	2.0
	0.93	0	38.4	<.001
	1.13	0	50	<.001
	0	4.7	43	0.2
	0	7.1	5	<.001
	0	10.2	<.001	<.001
	0.21	4.8	69	<.001
	0.60	4.9	<.001	<.001
Tull oil soap	0	0	4000	3500
Cottonseed soap	0	0	2200	1820

NOTE: These early results are erratic owing to lack of equilibrium, but are included since they do show differences in rate of breakdown as effected by water and free acid.

Summarizing, the normal method of preparation of Napalm results in a complex mixture of soaps which is self-peptizing and the addition of polar compounds to Napalm always results in a lowered gel viscosity. Conversely, the removal of these polar compounds raises the viscosity.

It will now be pertinent to examine some later data dealing with the less complex type of soap prepared from acids derived from a single source, as for example, sardine, cottonseed or tall oil. The less complex soaps do not gel at all readily when their water and free acid contents are low but, on the addition of polar compounds, however, they swell more and more readily in gasoline while the viscosities of the resultant gels first increase to a maximum and, thereafter, decrease in a manner similar to that shown by the above data on Napalm. The same effects are produced if, instead of adding free acids, the complexity of the soap is increased by incorporating soaps other than tall oil soap, for example, with the latter.

Effect on Gel Viscosity of Increasing the Complexity of Aluminum Soaps: 8% Gels in Shell Premium Gasoline

(Approximately 1% Water Content - Free Acid Less than 3%)

Aluminum Soap	Gardiner Viscosity	Remarks
(1) Stearate (Pure = M.P. of acid = 69.2°C)	0	Does not swell
(2) Oleate (Purer than USP Acid) (M.P. acid = 9.5°C)	0	" " "
(3) Resinate	0	" " "
(4) Tall Oil	170	Opaque, crumbly
(5) 90% Tall Oil, 10% Naphthenate	468	Cloudy, short, crumbly
(6) 80% " 20% "	610	" " "
(7) 60% " 40% "	830	Clearer than above, short
(8) 90% Tall Oil, 10% Oleate	330	Similar to naphthenate mixture (5) but less soluble
(9) 80% " 20% "	536	Similar to naphthenate mixture (6) but less soluble
(10) 60% " 40% "	816	Similar to naphthenate mixture (7) but less soluble
(11) 80% " (10% ") (10% Naphthenate)	780	Compare with 80 - 20 mixtures (6) and (9)

Effect of Added Free Acid on Gel Viscosity of Certain Aluminum Soaps

Aluminum Soap	Added Free Acid (Wt.% of Wt. of Neutral Soap Taken)	1 Week Gardiner Viscosities
Tall oil	No addition of free acid	170
	10% naphthenic	500
90% tall oil, 10% naphthenate	No addition of free acid	468
	10% naphthenic	666
	20% "	702
	10% oleic	603
	20% "	655
	10% tall oil	606
60% tall oil 40% naphthenate	No addition of free acid	634
	10% naphthenic	842
	10% oleic	894
	10% tall oil	894

All the above gels are short, the longest having an extensibility of only 0.3 inch but, nevertheless, the direction of procedure is indicated. Extensibility will be gained at a sacrifice of viscosity by further complicating the mixture or by adding more free acid. As a result of their high molecular weight, tall oil soaps require more peptizer than do the lower molecular weight sardine and cottonseed soaps. The latter, in particular, as would be expected from its composition, approaches Napalm in its properties quite closely even where no additives are present.

IV. Theory of Gel Structure. After summing up the pertinent facts concerning the chemical behavior of the aluminum atom, an hypothesis concerning gel structure may be advanced:

(1) The hydroxyl group of aluminum hydroxy dicarboxylates is too weak a base to combine with a third carboxyl group in true salt formation, particularly in aqueous solution. Compounds of the type $Al(OAc)_2OH.AcOH$, where Ac = acyl are known, but the third carboxyl group is connected by a co-ordinate, rather than by an ionic bond and is easily removed without hydrolysis. Compounds of the form $Al(OAc)_3$ may be formed under extreme dehydrating conditions but are of the character of acid anhydrides and, like these, are readily hydrolyzed.

(2) The aluminum atom possesses a strong tendency to co-ordinate with compounds containing an electron donor atom, usually oxygen or nitrogen atoms. By this donation of electrons the positive aluminum atom can form a tetrahedral structure, and become less polar. Some examples of electron donor compounds

which are applicable are water, carboxylic acids, alcohols, phenols, amines and, particularly, the carboxyl oxygens of the aluminum salts themselves. In the presence of more than one of these species, equilibria are established favoring combination with the compounds which co-ordinate with the greatest degree of avidity.

An assumption which now may be reasonably made from the above facts is that, in the absence of extraneous electron donors, the aluminum hydroxy dicarboxylate molecules link together in branched chains through carbonyl oxygen-aluminum co-ordinate bonds. The high molecular weight of such aggregates is evidenced by high melting point and general insolubility. That the said bonds are moderately strong is also concluded from the same properties. The fact that very little X-ray pattern is obtained indicates that the chain structure, once formed, is not permanent but is continually exchanging molecules between positions of attachment and thus shows little evidence of crystal structure. In order for this to be so, it must be assumed that, on the average, a small fraction of the molecules will be unco-ordinated at any given time and also, in order to account for some gel properties, that these individuals are soluble in non-polar solvents.

The final postulation is that if several carboxylic acids are used in the formulation of the aluminum soap, each molecular species present will exert its own escaping tendency practically independently of the others and thus the solubility of the mixture will be greater than any of its components. This has been shown to be the case in a non ionic medium for an homologous series when the materials are insufficiently soluble to change the properties of the solvent appreciably. An increase in the number of molecular species and, consequently, in the solubility may also be brought about by the addition of strongly co-ordinating compounds to the soap, but the effect on solubility is now still further enhanced as the polar compounds also compete with the soap molecules as co-ordinating agents for the aluminum atoms. Each time this happens, the molecular aggregate is broken down to a lower molecular weight. Since an aluminum atom co-ordinated with a phenol, for instance, is no longer available for chain building, there will be statistically more lower molecular weight fragments at any given time and, hence, a greater increase of soap solubility. A good example of this effect is shown in the process of oven drying of soap. Thus, wet samples of soap will sinter if brought to 160°F too rapidly, while if the same soap is dried more carefully it may be heated to above 200°F without sintering. When completely dry it will remain unsintered up to temperatures as high as 500°F, depending on its free acid content. Compared with water or an amine or a phenol, excess free acid produces a relatively small effect since aluminum co-ordinates with a carboxylic acid or with another soap molecule with about equal facility.

Examination of the data reveals the following changes in the behavior of aluminum soaps toward gelling solvents as the soap solubility increases:

A pure, dry aluminum soap made from a C.P. acid, e.g., aluminum hydroxy distearate, will not swell at all in gasoline. This remark should be qualified by acknowledging the fact that the solubilities of these pure soaps do differ and that, in general, the solubility increases in non-polar solvents as the molecular weight falls and approaches that of the C_{12} acids. An increase in solubility is also brought about by unsaturation of the acyl radicals. Soaps having acyl radicals which inhibit co-ordination by steric hindrance should also be quite soluble. However, such is not known to be the case. Now, as a polar compound is added to the soap or alternatively, as the complexity of the acyl radical mixture is increased, the soap will swell more and more readily up to the point where all the liquid is adsorbed in the gel structure. At this point the gel is short and crumbly and possesses low cohesiveness. Thereafter, the change may be followed by the change in viscosity and the increase in elongation allowed by the gel before rupture takes place. As the solubility increases, the viscosity rises to a maximum and thereafter decreases until a limpid fluid results. Such is the case where one equivalent of an amine has been added per mole of aluminum stearate. Near the viscosity maximum, the short gel begins to allow of greater elongation before rupture. Thus, it is possible to have two gels of like viscosity, one being short and the other long.

The above facts may again be explained on the basis of solubility. A short gel is presumed to have few mobile molecules in the solvent. On application of a distortional stress to the gel structure, partial rupture occurs and there is little chance for a free molecule to enter the gap and reestablish the chain. The force required to complete the rupture is now less than the original stress due to reduction in cross section and, therefore, the gel separates. The rate of shear plays a large part in the case of moderately short gels, for if given time, there may be sufficient reserve molecules in solution to repair the gaps or allow reorientation to relieve the strain. On the other hand, the long gels have plenty of reserve molecules and quickly compensate for impressed stress. To sum up, the mobility of the gel structure depends on the solubility of the soap in a given solvent, which in turn depends on the number of molecular species present.

The effect of change in solvent can be superimposed on the above behavior. In general, the soaps are more soluble in aromatics than they are in normal paraffins. Thus, dry Napalm will not gel in isooctane but will usually do so in benzol. Napalm plus 1.2 per cent water will gel desirably in isooctane and give a limpid solution in benzol. The total solvent effect on soap solubility is, however, less than that obtainable by changing the number of molecular species.

The element of time enters into the above comparisons and they are valid to the extent that all observations are made after equal time intervals from the time of mixing. Actually, the more soluble soaps go through all the stages from short gel to liquid as solvation proceeds, while the less soluble soaps reach equilibrium at some intermediate point. It is apparent that there must be sufficient molecular species in the soap to give a reasonably long gel and thus forestall breakup of the fuel in flight but, on the other hand, there must be insufficient to cause nearly complete solution and, consequently, lack of viscosity and gel structure.

The U. S. method of attaining this result has been to employ a complex mixture of acids, while the British prefer the method of adding polar compounds such as xylenols to a relatively pure soap. The result is similar but the U. S. method allows of greater tolerance of composition variations than does the British since small changes in the percentage of phenols added produce greater changes in gel characteristics than is experienced when soaps containing more or less free acids are used.

In a later section of this report the question of the oxidation of Napalm and its prevention by means of various inhibitors will be gone into at some length. As these inhibitors are polar compounds, a consideration of their effect on the properties of Napalm to which they have been added would appear to be logical at this juncture when the theories of gel formation and breakdown are under discussion.

All the so far discovered effective oxidation inhibitors for unsaturated aluminum soaps are polar compounds containing amino and/or hydroxy groups. As such, they are soap peptizers and, if added in sufficient quantity, will cause gel breakdown. However, it is now proposed to show that the conclusion that inhibitors are dangerous for this reason is not valid.

In the first place, the effect of all polar compounds in a soap is some additive function; that is, the added inhibitor, the water, the free fatty acids, the phenols, etc., present in a soap all contribute in varying degrees to gel breakdown. Therefore, one cannot say that, for example, one per cent of a certain added inhibitor will cause the breakdown of any Napalm sample. Recalling the effect of polar compounds on Napalm gels in first increasing and, thereafter, decreasing the viscosity while increasing the elongation, it is seen that in the case of short gelling soaps, a beneficial effect can result. It is also obvious that addition of an inhibitor to a soap, which is of such composition that it is already at the breakdown point, will certainly aggravate the situation. The remedy for this, obviously, is to manufacture soaps which, without inhibitor, would be of too high a viscosity, and then peptize them with the latter. This is, in part, analogous to the British method. Again the addition of an effective amount of inhibitor can be compensated for, in most cases, by drying the soaps more thoroughly.

Secondly, the tendency of inhibitors to cause gel breakdown will depend on the following properties:

(1) The avidity with which they co-ordinate with aluminum.

(2) Their percentage polarity; i.e., the fraction of the molecular weight per polar group. Thus, if a given weight of hydro quinone be incorporated in a soap almost twice as many hydroxyl

groups have been added thereto as would be introduced by the addition of the same weight of phenol.

(3) Their inhibitory effectiveness. If vanishingly small amounts are required, the contribution to gel breakdown will be negligible.

(4) Any peculiar molecular structure which they may possess which prevents gel breakdown. This will be discussed more fully later.

These variables may be indirectly evaluated by preparing a sample of soap, leaving one portion uninhibited and inhibiting the remainder. If viscosity measurements show that upon the addition of, arbitrarily, ten times the amount of inhibitor necessary for adequate oxidation stability, does not cause appreciable softening of the resultant gels, then the inhibitor may be considered safe. The factor of ten should be ample to take care of normal variations in the composition of the soap itself if measurements are made at constant water content. In the case of inhibitors which have to be coprecipitated with the soap, two separate soap batches are required and as a result, comparative measurements are much more doubtful. Variations of as much as 100 grams Gardiner cannot be ascribed to inhibitor breakdown unless consistent over many batches. Particular cases are considered below.

U.O.P. No. 5, recommended percentage, 0.01. 5 per cent gels, one uninhibited and the other containing 0.1 per cent U.O.P. No. 5 on soap weight, showed Gardiner viscosities after standing 10 days of 590 and 570 grams, respectively. One per cent U.O.P. No. 5 gave 340 grams, which may be considered breakdown. This compound can, therefore, be safely used as an inhibitor.

Lorene, N-dilauryl p-phenylene diamine; recommended percentage, 0.02. This is a homolog of U.O.P. No. 5 having about double the molecular weight of U.O.P. No. 5 and, this being the case, was not tested further in this laboratory. The California Ink Company, however, prepared a plant batch containing the above recommended percentage and the 24 hour heat test showed 555 grams on the blank and 555 grams on the inhibited samples. This material is, therefore, also to be considered safe.

Alphatol, a o-toluidine stearic acid; recommended percentage, 0.5. A soap gel containing 2 per cent water and no Alphatol showed about 40 grams Gardiner after standing 11 days. A similar gel made from soap containing 1 per cent coprecipitated Alphatol showed 500 grams at 11 days. A blank made from soap with 0.8 per cent water showed 600 grams and the same plus 5 per cent Alphatol, not coprecipitated, 520 grams at 10 days. (This procedure probably results in a corresponding increase in the free acid content of the soap.)

The line of reasoning which led to the synthesis of Alphatol is that if polar compounds cause gel breakdown by preferentially co-ordinating with the aluminum atoms and thus breaking chains, then this very effect might be put to use to prevent chain breaking. If the polar, inhibiting group is incorporated in a soap molecule, then co-ordination of the polar group to an aluminum atom other than the one in its own molecule will result in a continuation of a chain rather than in its termination because there is still a free aluminum atom to continue the chain. The data given above show that such is apparently the case. It is rather surprising to observe this result with Alphatol itself because alternative choices are possible. Owing to the position of the nitrogen atom with respect to the aluminum, a five membered stable ring can be formed by co-ordination of the two atoms. When this happens, polar properties are lost. Thus, the aluminum complex with Alphatol is a thick liquid, infinitely miscible with isopentane, which indicates lack of polar properties or high polymerization. If this structure were to persist on mixing aluminum Alphatol with Napalm, the net effect should be the same as adding, say lubricating oil, or in other words, no effect at all. Conversely, if one were to add considerable Alphatol acid to a Napalm gel, it might be expected that an equivalent amount of aluminum would be abstracted from the soap with the simultaneous release of soap acids. This should decrease the gelling effectiveness of the soap. All three processes can be detected in the above data, but apparently the first process, resulting in a more water resistant gel structure predominates when the Alphatol is coprecipitated with the soap. Alphatol can be considered a safe inhibitor and the only possible objection to its use is a slight increase in cost due to the relatively large amount necessary to give adequate inhibition.

Alphanil, a (p-oxyanilino) stearic acid: recommended percentage 0.10 - 0.15. Before a 150° heat test apparatus was assembled, the following tests were made at room temperature on soaps containing water and Alphanil in varying amounts.

Effect of Alphanil on Gel Viscosity
8% of Napalm with Coprecipitated Alphanil in Shell Premium Gasoline

% Added Alphanil	Approximate Water %	1 Week Gardiner Viscosity
0	0.9	490, 507
0.1	1	505, 530
0.5	1	520, 530
1.0	1	490, 510
5.0	1	650, 650
0.1	0.8	640, 624
0.5	0.8	661, 670
1.0	0.8	670, 658
5.0	0.8	750, 772

Thus it is seen from these cursory experiments that, when a slight variation in water content is allowed for, Alphanil has no effect on gel viscosity until between 10 and 30 times the amount required for satisfactory inhibition has been added, at which point a stiffening effect appears. These results are not conclusive, however, as heat tests at 150° are not included.

Later, heat test apparatus was built, but in the interim the acid supply available was depleted and fresh material had to be obtained from the California Ink Company. All of the soaps made from this, including the blanks for which the data are tabulated below, give very soft gels. Thus, conclusions about the effect of Alphanil are doubtful and further tests would have to be made before its use can be recommended with certainty.

Behavior of Some Napalm Gels under the 150° Heat Test
(Gardiner instrument calibration C.S-201A = -21 grams)
8% Gels in Shell Premium Gasoline

Per Cent Water	Per Cent Alphanil	Gardiner Viscosity 150°F Heat Test 2 Hrs.	24 Hrs.
0.5	0	370,329	206,256
0.8	0	213,214	204,253
1.2	0	189,196	-
0.8	0.1	-	207
0.8	0.5	342	-
0.8	1.0	404,450	206,240
0.8	5.0	205	-

The same soap, but containing 0.1 per cent of α-naphthol, gave 329,344 at 2 hours and 279,289 at 24 hours.

An oxidation test on the blank sample showed it to be very stable toward oxidation. This leads one to suspect that the naphthenic acids in this particular soap contain far too much alkyl phenols.

Pending receipt of a different sample of naphthenic acids from Standard Oil of California, a makeshift run was made by testing an 8 per cent gel of Nuodex Napalm, No. 17965, 0.8 per cent water, in gasoline and comparing with the same soap which had one per cent of Alphanil added to the gasoline in which the soap was gelled. Since the Alphanil dissolves in gasoline extremely slowly, it was dissolved hot in 3 cc. of naphthenic acids and then added to the gasoline. No precipitation occurred, and the gel was then made up in the usual manner. The results of the 24 hour heat test are 424,434 on the blank and 489,442 on the sample containing Alphanil. These results thus indicate that the Alphanil has no deleterious effect on the gel.

Repeating the previous tests on coprecipitated Alphanil, but with a different sample of naphthenic acids, 24 hour heat tests on 8 per cent gels showed:

Blank - 0.8% H_2O	403 grams
0.5% Alphanil - 0.78% H_2O	595 grams
1.0% Alphanil - 0.8% H_2O	395 grams

Since all blanks and samples containing 1 per cent Alphanil give essentially the same viscosity, these results show that the material is satisfactory. This has also been confirmed by stable plant batches made by Ferro Enamel and the California Ink Company.

In conclusion, it may be said that practically any inhibitor may be added to a normal soap in up to 0.1 per cent concentration without fear of gel breakdown. Should breakdown occur, it is not the fault of the added inhibitor but rather that the soap in question, due to improper preparation, is itself on the point of breakdown. The value of adding this 0.1 per cent of inhibitor will, of course, depend on whether or not this amount is adequate to stabilize the soap.

V. Inhibition of Oxidation of Napalm Soaps. One of the greatest difficulties in connection with the use of Napalm is that the material is exceedingly liable to oxidation (owing to the unsaturated compounds present), both in the course of manufacture and in subsequent storage. As this oxidation proceeds, solvation of the material in gasoline becomes more and more difficult, the resulting gels being more viscous and, at the same time, show a drop in extensibility. The problem of preventing this oxidation by the addition of various inhibitors was, therefore, taken up. The methods of experimentation and the results obtained will now be described in some detail as the problem is considered to be one of paramount importance if, as seems likely, the material is to be used on an extensive scale.

The oxidation of Napalm during storage, which results in materials of slow or infinite setting time and short gels, may be inhibited completely for the anticipated maximum storage time of six months at 130°F. The inhibition is accomplished by the addition of UOP No. 5 inhibitor or its more satisfactory homolog, dilauryl para phenylene diamine, α-ortho toluidino stearic acid or Alphanil (α(p-oxyanilino) stearic acid). The choice between the four will depend on availability and the method of incorporation desired. The diamines are sprayed on the precipitated soap before drying while the stearic acid derivatives are added to the sodium soap solution and coprecipitated as an integral part of the Napalm.

Experimental Method

The method of testing aluminum soap products for oxidation stability introduced here has been adapted from that used in the testing of gasolines and consists in subjecting the soap to the action of oxygen in a bomb under elevated pressure and temperature. The UOP test bombs used*

---

* Egloff, Morrell, Lowry and Dryer. Ind. Eng. Chem. 24, 1375 (1932).

were modified to include a 200 psi. safety disc to protect the recorder.

Fifteen gram soap samples are placed in 8 ounce polished oil sample bottles and inserted in the cold bombs. Nitrogen is swept out of the system by admitting oxygen to 100 psi. and releasing the pressure. This is done twice and then the pressure is brought to the desired value. The bombs are then heated to the required temperature which is maintained by the thermostated oil bath and allowed to run until a rapid absorption of oxygen occurs as indicated on the chart or by bursting of the popoff disc. A correction of 45 minutes is subtracted from the total time to allow for the heating up period. This correction was determined from the heating up time-temperature curve and the appropriate equation shown elsewhere in the report. By varying the pressure and temperature of the tests, the dependency of the duration of the induction period on these variables was obtained for the most promising inhibitors and extrapolations made to storage conditions.

As disclosed elsewhere*, the samples used in the bomb tests are made in a special manner to prevent sintering in the bombs. In event of sintering, the rate of oxygen absorption is governed by its slow rate of solution in the soap rather than by the speed with which it actually reacts and no satisfactory induction period is obtained. Since excess free fatty acids are responsible for the sintering, the soaps were made up in the following manner:

> A one normal solution of basic aluminum sulfate is added slowly with very rapid stirring to an equivalent (equal volume) amount of neutral one normal sodium soap solution. The very fine precipitate produced at first remains dispersed in the excess soap solution until just before the endpoint when the particles coagulate. After washing and drying, the soap still contains 3 to 10 per cent free acids extractable with acetone. The soaps at the lower figure are usable directly in the bombs but those containing above 6 per cent free acid must be extracted with acetone before testing. The acetone not only removes free acid but also neutral oil and alkyl phenols, both of the latter being introduced by way of the naphthenic acids. (See discussion.) The samples are then screened through 30 mesh, inhibited if the inhibitor is to be applied by spraying, redried and tested.

Reproductions of some typical recorder charts are shown in Figure I.

Experiments and Discussion.

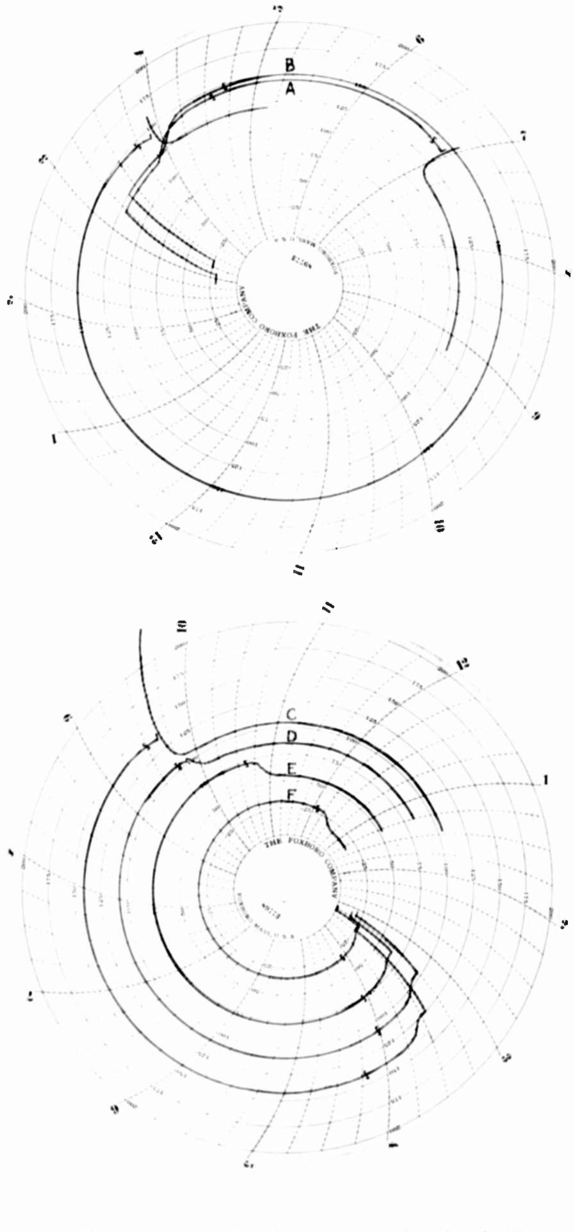
At the start of this investigation it was realized that the material responsible for the oxidation instability of Napalm soaps was aluminum oleate rather than the saturated components but to prove the point, samples

---

*Monthly Reports on Contract 11-394 - OEMsr-916, Problem CWS-10, February 15 - March 15, 1943 and March 15 - April 15, 1943

FIGURE I
Illustrative Charts from the Accelerated
Oxidation Test Apparatus

Time vs. Oxygen Pressure (Psi. Gauge)



Curve A – Straight Napalm 135 min. standard IP.
" B – Sample A + 0.01% UOP#5, 662 min. standard IP.
" C to F – Sample A at 80°C and 25, 50, 75, and 100 psi. O_2.
Variation of IP and violence of reaction with pressure.

of pure aluminum oleate and of aluminum stearate were prepared and tested at 100 psi. oxygen pressure and 100°C which henceforth is called "standard test". The induction period of the oleate was 20 minutes and that of the stearate infinite, no change occurring in the properties of the latter during a test period of 46 hours.

No Napalm acids were on hand and rather than wait for the receipt of these, research was continued using an aluminum talloil soap, brand name "Bogel", which, owing to its unsaturated character, possessed the desired instability. The standard induction period, I.P., for this material was 20 minutes. This soap was precipitated from solutions containing an excess and a dearth of caustic over the theoretical to examine a suspected variable. The two samples, however, did not differ in induction period but only in the violence of the reaction at the end of this period. The sample precipitated from the acid mother liquor sintered slightly in the bombs owing to excess fatty acid and hence showed a less rapid reaction. Tests also showed no dependence of the duration of the induction period on particle size as long as the latter was 8 mesh or less.

Spot tests were then run on several inhibitors commonly used with unsaturated materials. The results are shown in Table I. Later spot tests on Napalm are included for convenience in Table Ia.

At least one member of each of the common inhibitor types is represented in the table. The indications are that inhibitors effective in gasoline are also effective in aluminum soaps although they are not rated in the same order in the two cases. On the other hand, rubber and lubricating oil inhibitors are not as effective. At the time the tests in Table I were run, UOP No. 5 was obviously the best tried, so further work was confined to this material.

TABLE I

Spot Tests on Inhibitors
Inhibition of the Oxidation of Aluminum Talloil Soap
Standard Test - 100°C and 100 Psi. O_2 (Gauge)

Inhibitor	Amount Added to Soap Reactants, % Based on Soap Yield	IP (Minutes)
None	-	20
Hydroquinone	1*	25
du Pont No. 19	1	150
Lecithin	1	20

* Considerable loss to mother liquor owing to solubility of inhibitor in same.

TABLE I CONTINUED

Spot Tests on Inhibitors
Inhibition of the Oxidation of Aluminum Talloil Soap
Standard Test = 100°C and 100 Psi. O_2 (Gauge)

Inhibitor	Amount Added to Soap Reactants, % Based on Soap Yield	IP (Minutes)
SPC	1	345
Rubber inhibitor composed of phenyl α and β naphthyl amines	1	97
α-Naphthol	1*	307
2,4,6-Trimethylphenol	1	95
2,4-Dimethylphenol	1	63
2,4,5-Trimethylphenol	1	49
2,4-Dimethyl-6-butylphenol	1	70
3,3',5,5'-Tetramethyl-4,4'-dihydroxy diphenyl	1	17
Santolene A	1	53
UOP No. 5	1*	519
Aerohib	1	64
Floyd's base No. 28	2	1
Aerolube EU	1.49	21

* Considerable loss to mother liquor owing to solubility of inhibitor in same.

TABLE Ia

Spot Tests on Inhibitors
Inhibition of Napalm
Standard Test

Inhibitor	Additional Soap Treatment	IP (Minutes)
None	None	205
0.1% N-phenyl N'-dihydroisophoryl thiourea*	None	195
None	Acetone extracted	50
1% Alphatol (α-ortho toluidino stearic acid)*	"	300
1% α(para-amino anilino) stearic acid*	"	410
0.25% α(para-oxyanilino) stearic acid*	"	1225
0.1% N-octadecyl para-amino phenol +	"	830
0.02% N-dilauryl para-phenylene diamine +	"	780 (96.7°C)

* Coprecipitated

\+ Sprayed on soap granules

As stated before, samples high in fatty acids must be extracted with acetone before testing to prevent sintering. A clue to what other effect this has is seen in Tables I and Ia. Talloil soap shows the same induction period as does aluminum oleate, but unextracted Napalm has about a ten-fold induction period. However, after 3 extractions with 5 times the sample weight of acetone, the oxidation time of Napalm approaches the others. If the extraction were complete, all three soaps would show the same induction period.

Obviously, Napalm, as ordinarily prepared, already contains an inhibitor which is removable by acetone. This was proved by incorporating the extract, after removal of fatty acids, into a talloil soap in the same proportion at which it was removed from Napalm, namely, 1.6 per cent. The induction period of this sample was then found to be increased from 120 to 660 minutes at 80°C and 100 psi. oxygen pressure. The lower temperature was used to prevent undue sintering in the bombs. The comparative behavior of the acid free extract in gasoline indicates that it is composed of about 25 per cent of full range alkyl phenols, the rest being neutral oil, or, calculating back, there was 0.4 per cent of these alkyl phenols in the original Napalm. Their odor and physical properties indicate that they were introduced via the naphthenic acids. A rational suggestion would be to stabilize the soap by a further addition of these phenols but actually it is found that in order to do so the concentration of phenols must be so high that they would lead to break down of the gel. As to the validity of runs made on extracted samples, it is seen that the error in so doing is on the conservative side and that actual samples which, of course, will not be extracted will be more stable than the extracted samples reported as a result of the synergistic action of the two inhibitors. The above data are compared in Table II.

TABLE II

Comparison of Oxidation Stability of Several Aluminum Soaps and Tests on the Napalm Natural Inhibitor

Sample	Temperature °C	Pressure Psi. O_2 Gauge	IP (Minutes)
Oleate	100	100	20
Stearate	100	100	∞
Talloil (Bogol)	100	100	20
Napalm	100	100	205
Extracted Napalm	100	100	50
Talloil	80	100	120
Talloil + Napalm extract	80	100	660
Gasoline A	100	100	85
Gasoline A + 0.02 g./100 cc. acid free Napalm extract	100	100	103
Gasoline A + 0.02 g./100 cc. 220-240° alkyl phenols	100	100	230
Unextracted Napalm + 0.01% UOP No. 5 Sprayed on	100	100	1470
Extracted Napalm + 0.01% UOP No. 5 Sprayed on	100	100	650

Accelerated tests at one temperature and pressure do not give a quantitative answer to the question of the storage stability of a material but, by taking measurements at several temperatures and pressures, an equation may be derived for each material and from it, an extrapolation made to the desired conditions. As is the case with gasolines, the logarithm of the induction period was found to be proportional to the reciprocal of the absolute temperature and to the logarithm of the absolute pressure. For extracted Napalm soap the equations are:

$$\text{Log. IP (min.)} = \frac{5480}{T} - 13.001 \text{ (at 25 psi. } O_2 \text{ gauge)}$$

$$\text{and Log. IP (min.)} = 3.021 - 0.556 \text{ log. P (at 98.6°C)}$$

From these equations, the following conversion factors can be deduced:

> One minute at 100°C is equivalent to 0.00213 months at 130°F and one minute under an oxygen pressure of 100 psi. gauge is equal to 7.6 minutes at one atmosphere of air. Thus, 6 months at 130°F and one atmosphere of air is equal to 370 minutes of standard test.

When the above Napalm is sprayed with 0.01 per cent UOP No. 5 in acetone or as a solution of its acetate in water and thereafter dried, the equations become:

$$\text{Log. IP (min.)} = \frac{5630}{T} - 12.419 \text{ (at 100 psi. } O_2 \text{ gauge)}$$

$$\text{and Log. IP (min.)} = 4.295 - 0.717 \text{ log. P (at 96.7°C)}$$

and the factors are:

> One minute at 100°C is equivalent to 0.00246 months at 130°F and one minute at 100 psi. oxygen (gauge) corresponds to 12.68 minutes at one atmosphere of air or 6 months at 130°F is equal to 192 standard minutes. Since an uncertainty of 25 per cent may occur in the above extrapolations, the necessary times at standard test have been increased 50 per cent for a factor of safety. The test data for the above equations are given on page two of the report for March 15 - April 15, 1943*.

From storage tests it was found that Napalm sprayed with up to one per cent UOP No. 5 did not break down but it must be remembered that the action of water, of the natural inhibitors and of UOP No. 5 are all additive. Hence, samples which are just on the point of water breakdown or which are high in alkyl phenols will not tolerate much UOP No. 5. Therefore, the use of more than 0.1 per cent UOP No. 5 is not to be recommended, especially as 0.02 per cent will stabilize the average soap with a large factor of safety when applied after precipitation.

* Monthly Report on Contract 11-394 - OEMsr-916, Project [illegible]-10.

At this point it may be mentioned that one so far uncontrolled factor contributing to variability in Napalm, both with regard to oxidation stability and to gel breakdown, is the alkyl phenol content of the naphthenic acids used, both the amount and the type being important. Control of this variable may be effected by specifying that when, say a 50-50 mixture of a sample of the batch of naphthenic acids in question with fresh oleic acid is submitted to an accelerated induction period, a definite induction period shall result.* Until this is done, any certainty of the oxidation stability of Napalm, with or without inhibitors, cannot be expected. At the same time, adjustment of the results of the tests by the use of additives should be prohibited, since this would void the estimation of the natural inhibitors present. Rather, the desired constancy of stability should be attained by using a single raw material source and a constant method of isolation.

Since the use of UOP No. 5 will permit extended drying periods or elevated drying temperatures without oxidation difficulties, any tendency for UOP No. 5 to cause gel breakdown may be counterbalanced by drying the soap more thoroughly. This fact has been observed by California Ink Company who have been inhibiting their plant batches with 1 per cent β-naphthol. Before the inhibitor was used, their gels did not soften on storage when the soap contained 1 per cent water. After inhibition was started, the soaps had to be dried to 0.3 per cent water to prevent breakdown.

UOP No. 5 can also be added to the soap solution before precipitation but then almost 0.1 per cent must be used since the inhibitor is then evenly distributed throughout the soap granules and therefore has a lower surface concentration where its action is important. A compromise between this method and spraying is to add the inhibitor after precipitation but before filtering. Then it will partition itself between the soap and the mother liquor, the completeness of adsorption by the soap granules depending on the pH of the mother liquor since UOP No. 5 is slightly soluble in water and very soluble in acidic solutions. To overcome this latter difficulty, "Lorene", N-dilauryl phenylene diamine, is proposed. In a concentration of 0.02 per cent, this material is slightly superior to UOP No. 5 on a molal basis, the standard induction period being 780 minutes and, moreover, it has the advantage of being insoluble in water or dilute acids and of being strongly adsorbed by the soap pulp. It can either be added to the precipitation vats after that operation is complete, without loss to the mother liquor or sprayed on after filtration.

All of the inhibitors discussed above are polar compounds and, as such, have the disadvantage that a quantity sufficient to cause gel breakdown may be added to the soap, although there is no reason for doing so with the more powerful examples. Nevertheless, it is felt that it would be desirable to have an inhibitor which was free from this action.

---

* See Section VII.

As a working hypothesis, it is assumed that the polar groups interfere with the normal chain building mechanism of co-ordination of the aluminum atom of one molecule with a carboxyl oxygen of the next. Since aluminum co-ordinates more powerfully with amino or hydroxy groups than it does with carboxyl oxygen, preferential saturation of the aluminum atoms with the former species will break the chains and result in gel breakdown arising from the increased solubility of the lower molecular weight units. This tendency should be overcome by including the inhibitor as a substituent in a soap molecule. Then any increased tendency to co-ordinate owing to the polar groups will continue the chains instead of breaking them. This addition will then result in a stiffer gel. If, however, the polar groups are so situated (e.g., alpha to the carboxyl) that they preferentially co-ordinate with the aluminum atom in their own molecule then the additive will be inert and produce no change in the final viscosity of the gel. The indications are that the above is actually the case.

α-Ortho toluidino stearic acid, Alphatol, prepared by heating α-bromo stearic acid with an excess of ortho toluidine, forms a basic aluminum salt which is a thick liquid at ordinary temperatures and is infinitely soluble in non-polar solvents. Thus, owing to internal co-ordination (chelation) there is no tendency for the material to associate.

In preparing a soap inhibited with Alphatol, one per cent of the substance based on final soap yield was added to a neutral sodium soap solution which was then reneutralized. The whole was precipitated with basic aluminum sulfate and the precipitate acetone extracted as usual. This soap had a standard induction period of 300 minutes which is ample provided no marked change in the pressure coefficient has occurred. This, however, remains to be investigated.

Ortho toluidine itself is not a very effective inhibitor but is rendered somewhat more so by its substitution into stearic acid. Work has also been done on the analogous substitution of some of the better inhibitors. One outstanding compound is α-(para-oxyanilino) stearic acid (Alphanil) made from para aminophenol. The induction period of Napalm with 0.25 per cent of this material coprecipitated is 1225 minutes. However, it contains two polar groups one of which may chelate with the aluminum atom in its own molecule and the other with an adjacent aluminum atom. Since its own aluminum atom is no longer available for chain building, the net result may be the same as if a plain phenol were used.

To determine the concentration of α(p-oxyanilino) stearic acid, required to adequately stabilize the average Napalm, the following figures were obtained and the usual equations set up:

Sample	Temperature C°C	Oxygen Pressure psi. gauge	IP (Min.)
Acetone extracted Napalm plus 0.1% Alphanil	100	100	195
	100	75	222
	100	50	255
	100	25	310
	89.8	100	525
Acetone extracted Napalm plus 0.15% Alphanil	100	100	395
Unextracted Napalm plus 0.15% Alphanil	100	100	750

The equations are:

$$\text{Log. IP (min.)} = \frac{5704}{T} - 12.999 \text{ (at 100 psi. } O_2 \text{ gauge)}$$

$$\text{and Log. IP (min.)} = 3.1900 - 0.4369 \text{ log. P (at } 100°C)$$

Thus, each minute at standard test is equivalent to 0.0152 months at 130°F and the partial pressure of oxygen in the atmosphere (2.94 psi.). The required induction period is therefore 395 minutes at standard test. It is seen that 0.15% Alphanil will do this in the worst possible case of the extracted sample. Unextracted samples will, of course, require less added inhibitor as they already contain varying amounts of inhibitor (alkyl phenols). It is seen from the table that an unextracted sample shows approximately a two-fold increase in induction period over the extracted sample containing the same amount of added inhibitor. A plant batch made by the California Ink Company containing 0.1 per cent Alphanil ran for more than 24 hours without change.

As far as is known this type of calculation has never been carried out on a naphthol. After the first spot test, no further work was done here because this material is quite soluble in the soap mother liquor and, at the same time, inferior to UOP No. 5 in inhibiting action. However, if it is to be used, it is suggested, in the interests of economy, that the usual quantitative data be obtained as soon as possible.

Some clue to the mechanism of the process whereby the absorption of oxygen by a soap results in a loss of the gelling action of the latter can be deduced from the following data and from a similar case recently reported by Cowan & Wheeler (J.A.C.S. 66 84 1944).

Two samples of soap were made up, a blank and one containing 0.1 per cent Alphanil, both being non-extracted. These soaps, together with a sample of Ferro Enamel, Batch No. 532, containing α naphthol, were subjected to accelerated oxidation at 100°C and 100 psi. oxygen in the UOP type bombs for 65 hours. Naturally, no induction periods were obtained due to the normal fatty acid content and resultant sintering. At the end of this time, the two inhibited soaps had absorbed about one psi. of oxygen each and the blank, 10 psi. Assuming peroxide addition of a mol of oxygen per double bond in the soaps, these figures would represent 10, 10 and 100 per cent peroxidation of the double bonds present. Actually, the drop in iodine values were 4.4% for Alphanil, 5.7% for α naphthol and 8.9 per cent for the blank. Moreover, the two inhibited samples would still gel in gasoline whereas the blank would not.

From the above, it is obvious that the peroxides initially formed break down during the test and higher oxidation of the resulting fragments occurs. This fact is substantiated by the presence of aldehydes and maladorous fatty acids in soaps which are only slightly oxidized. That the peroxides are transient is evident from the fact that if a stable peroxide like benzoyl peroxide is added to a Napalm gel, the latter soon becomes granular and synerizes - the typical effect of oxidation.

Since the introduction of more polar compounds (oxidation products) into a soap by this oxidation should result in a gel breakdown effect instead of the production of a non-setting soap it is suspected that higher polymerization due to cross-linking, rather than oxidation itself, is responsible for loss of gelling ability.

Cowan & Wheeler found that they could produce straight chain polymers from unsaturated dibasic acids and glycols only in the absence of oxygen. (The typical indications of chain polymers are gelling ability with high polymers and solvent solubility with the lower ones.) If oxygen was admitted to the system the chains became cross-linked by means of covalent bonds giving a space network, a defining characteristic of such a network being general insolubility in solvents. In addition, chain structures generally possess a melting point whereas the space networks do not melt.

The case under consideration is not exactly analogous because, although composed of chains in the main, there are also weak co-ordinate cross-linkages (presumably hydrogen bonds) which give the soaps a psuedo space network characteristic, as is evidenced by the high melting points of pure soaps. Nevertheless, when these weak bonds are replaced by covalent linkages a true space network results and the product becomes insoluble.

If the term polymerization may be used for this process on an already polymerized material, then it may be said that polymerization catalyzed by peroxides is the cause of loss of set.

It is also seen that measuring the oxygen absorbed does not measure directly the value of a soap as a gelling agent, although, of course, a soap which resists oxidation will also resist polymerization. Owing to the transient nature of the peroxides formed under accelerated conditions, measuring the amounts of these also does not necessarily give a true indication of the state of a soap. Probably the most direct measurement would be of the unsaturation of the material. In this regard, it may be stated that iodine values determined by means of Wij's reagent are valid only on unoxidized material since aldehydes interfere under present conditions of test to give high values for double bond content. Thus, a sample of propionaldehyde reacted to give an α mono halogenated aldehyde to the extent of 80 per cent under the conditions of test, at the same time releasing hydrogen halide.

VI. Effect of Iron Content on the Oxidation Stability of Napalm. To date it has been found that Napalm samples made from different lots of naphthenic acids possess variable susceptibility to the catalytic action of iron soaps. Consequently no general statements can be made concerning the maximum tolerable amount of iron, since this quantity varies with the history of the soap. For example, one sample remained unoxidized for 300 minutes standard test in the presence of 0.05 per cent iron and without inhibitor. The addition of 0.01 per cent UOP No. 5 raised this tolerance to 0.1 per cent. Another sample broke down long before this time though its iron content was only 0.004 per cent. With addition of 0.01 per cent UOP No. 5, the same sample barely passed at 317 minutes.

An acetone soluble iron deactivator is apparently present in Napalm, since extraction of the soap with that solvent reduces the stability in the presence of 0.025 per cent iron to practically zero, if uninhibited, and to 150 minutes with 0.01 per cent UOP No. 5 added. This deactivator may or may not be identical with the natural alkyl phenols.

Considerable iron may be incorporated in the soap via the oleic and naphthenic acids since both of these are found to deposit iron soaps when made into sodium soap solutions. As the coagulated iron may be filtered out nearly completely after the sodium solutions have stood for 24 hours, there would appear to be no necessity to include this iron in the product.

It is evident that the adverse effect of iron can be compensated for by the addition of inhibitors but, in the interests of economy, the iron content should be kept at the lowest possible figure.

VII. Specifications for Naphthenic Acids. At the start of this problem, a few exploratory experiments were run on a sample of oleic acid and one of naphthenic acids obtained from Nuodex. Both the acids contained the same per cent of iron, namely, 0.017 per cent. This iron was removed from a portion of each by converting the acids to sodium soaps and filtering. On springing the acids with iron free hydrochloric acid the iron content was reduced to about 7 x 10^{-5} per cent.

Standard induction periods on the oleic acid were 30 minutes for the contaminated sample and 60 minutes for the iron free sample. The addition of the iron free sample of naphthenic acids to the iron free oleic acid in concentrations of 4,8,16 and 24 per cent increased the induction period of the oleic acid to 2.5, 3.9, 5.3 and 7.5 hours. It is expected that the effect of iron on these values will be much greater than in the case of the uninhibited oleic acid. It is not considered that the naphthenic acids themselves have any effect, other than as a diluent, on the induction period. They are regarded as a carrier for the alkyl phenols and peroxidants simultaneously introduced.

As it was found that the induction period was independent of the total amount of sample, 10 to 100 grams giving the same induction period, a standard mixture of 4 grams of naphthenic acids in 21 grams of oleic acid was adapted for the sake of obtaining reasonable induction periods. Three samples of acids from Oronite Chemical Company and the current Naphthone "M" from California Ink were compared and the results are shown below.

Sample	Iodine Value of Naphthenic Acids	% Neutral Oil in Naphthenic Acids	I.P. Hrs.
Iron Free Oleic Acid (I)	-	-	0.5
(I) + 16% Naphthone "M"	-	-	3.2
(I) + 16% Crude Oronite Acids	14	7.3	6.5
(I) + 16% Semi-refined Oronite Acids	12	4	9.5
(I) + 16% Refined Oronite Acids	6	3.6	24

The iron, phenol and nitrogen base contents of the acids are unknown. The crude sample is the entire caustic extract of the base stock, the semi-refined is the re-extracted caustic extract (removes some neutral oils, weak acids and bases) and the refined material is the acid treated semi-refined extract (removes some unsaturation, some metals, some aromatic derivatives and most of the colored impurities). The two refining operations should remove a part of the alkyl phenols present and thus decrease the induction period. However, at the same time nitrogen bases and unstable unsaturates are also partially removed which results in a more stable product.

For this test to be of any value, the relative stability of these acid mixtures should agree with the relative stabilities of Napalms made from the several samples. To test this, the Napalms were made up from 15.3 grams of the acid in question, 24.4 g. coconut acids and 21.4 g. oleic acid according to established procedure. Because of sintering, these soaps did not show an induction period and they were inspected for iodine value after standard test conditions for 65 hours.

Sample	Original Iodine Value I	II	III*	Iodine Value after 65 hr Standard Test I	II	III*	Δ Iodine Value I	II	III*
Napalm made with Naphthone "N"	36.3	36.4	36.2	10.1	8.4	0	26.2	28.0	36
Napalm made with crude Oronite acids	37.9	(39.3)	37.4	32.3	28.5	36.9	5.6	-	0.5
Napalm made with semi-refined Oronite acids	38.8	38.9	38.9	36,0	26.6	34.6	2.8	12.3	4.3
Napalm made with refined Oronite acids	38.2	36.2	36.1	8.4	9.1	0	29.8	27.1	36

* Iron in acids not removed by filtration of sodium soaps as was done in I and II which are duplicate batches.

These data are erratic, but do differentiate between the crude and the semi-refined acids on the one hand and the refined and the Naphthone "N" on the other. A comparison of these two tables will show that the free acids and their respective aluminum salts are rated in a different order of stability, which is not entirely surprising if one takes into account the changes in the redox potentials of inhibitors with any change in state of the electrons situated on the polar oxygen or nitrogen atoms of the inhibitors. The change in effectiveness of inhibitors on substitution of the nitrogen atoms was discussed under the section on Alphatol and Alphanil. A similar effect will be noted in the present case on conversion of the free acids to aluminum soaps. On so doing, the phenols present will co-ordinate with the aluminum atoms by partial transfer of a pair of electrons. This will tend to throw a more positive charge onto the oxygen and facilitate removal of the OH hydrogen, thus lowering the oxidation-reduction potential. Since inhibition probably depends on a proper and fine balance between the respective potentials of the inhibitor and of the inhibited material, a change of potential of an inhibitor already in fine balance will partially destroy its effectiveness.

At the same time, a relatively ineffective inhibitor present in large amounts compared to the effective inhibitor, may become effective when the potential change occurs. Thus, it may be explained why the free acids and the aluminum soaps made from these acids behave differently when subjected to oxidation.

The results indicate that a specification test run on the free acids does not give any information as to the stability of aluminum soaps made therefrom and, therefore, some other method should be adopted.

VIII. Determination of Water in Napalm. The standard method used in this laboratory for determining water is that of Fischer, described in J.A.C.S. 61, 2407 (1939) with the exception that 80 - 20 glycol-pyridine is substituted for the methanol as solvent. Glycol pyridine mixture (10 cc.) was added to a 50 cc. volumetric flask and brought to an end point with the reagent. Next, 1.612 grams of Nuodex Napalm were added and, after 5 minutes shaking, the titre was found to be 2.9 cc. After 45 minutes a further 1.5 cc. was added but the end point continued to fade rapidly. On repeating the process with 10 cc. of glacial acetic acid added in addition to the glycol-pyridine, 2.114 grams of sample titred 6.40 cc. after 5 minutes, plus 3.95 cc. at 45 minutes, plus 0.55 cc. at 50 minutes giving a total of 3.19 per cent water. Heating on a waterbath for one hour before titrating gave a figure of 2.95 per cent for the water content but none of the above end points are stable for 30 minutes. When 10 cc. excess reagent was added and the mixture back titrated with standard water in methanol the result was 3.48 per cent. Finally, if the sample was gelled first in 20 cc. of toluene and then broken down to a limpid fluid with 5 cc. of pyridine, glycol-pyridine added and finally titrated, the water content obtained was 3.56 per cent. This determination can be run in one hour, once the reagents are made up. A blank is run in an identical manner, adding all materials except the sample. The end point obtained in this way is sharp and permanent provided that the soap has been well dispersed.

An azeotropic distillation of the same sample with benzene was carried out as follows. A 500 cc. flask containing 200 cc. dry benzene and a Soxhlet thimble were connected to a 3 foot column packed with glass beads. Distillation at 10 to 1 reflux was carried on until the distillation temperature reached 80.5°C. The flask was then quickly disconnected and 2.762 grams of sample dropped into the thimble. Distillation was resumed until the temperature rose again to 80.5° and held there for 15 minutes. The distillate was collected in a 250 cc. volumetric flask containing 10 cc. of glycol-pyridine previously brought to the dry point with Fischer's reagent. The contents were then titrated giving 1.63 per cent water in the soap. Use of the thimble prevents burning of the soap on the bottom of the flask when electric heat is employed.

The following table shows the data obtained on a different sample prepared here.

Method	Per cent Water found	Remarks
1. Vacuum drying at 100°C and 2mm. pressure	1.0	Probably consists of most of adsorbed water and separation of doubled molecules of hydration.
2. Dean and Stark with toluene or benzene	2.8	Above water plus that from a lesser degree of hydration and some water of reaction due to duration of process.
3. Azeotropic distillation with dioxane	2.5	Employed to avoid the inevitable water hold-up in apparatus and consequent lengthening of time of analysis. Distillation over in 30 minutes instead of 4 hours. Fischer or acetyl chloride methods used to determine water in distillate.
4. Fischer method as described in JACS 61, 2407, (1939)	2.1 - 3.0	End points fade and procedure is time consuming due to lack of dispersion of sample in solvent and resultant slow reaction.
5. Fischer modified by gelling sample first in toluene and then breaking down to a liquid by addition of pyridine	3.7	End point definite and fairly rapid. Water value probably includes some water of reaction due to extreme dehydrating conditions.
6. Fischer method on residue of dioxane distillation	1.2	Total of 3. and 6. equals 5.
7. Acetyl chloride-pyridine method. JACS 57, 841 (1935) Modified	1.1 - 1.2	Acetyl chloride treatment at 25°C, 5 to 40 minutes duration.
	1.9 - 2.1	Acetyl chloride treatment at 60°C, 5 to 40 minutes duration.
	4.0 - 4.2	Acetyl chloride treatment at 80°C, 5 minutes duration. Samples turned brown - obvious decomposition of soap.

The dioxane distillation referred to in the foregoing table was carried out in the same apparatus as the benzene distillation but without the thimble and 25 grams of sample were used in order to get an appreciable amount of distillate. The acetyl chloride method is obviously arbitrary and unsatisfactory.

From the foregoing it would appear that the choice of the method to be used for water estimation would seem to be a matter of personal preference, as comparative figures for water estimation may be obtained on several soaps by any of the above. The Fischer procedure probably gives the absolute water content, including water produced by completion of the neutralization reaction. On the other hand, the figure obtained either by azeotropic distillation or vacuum drying probably more nearly represents the water responsible for co-ordinate bond formation. In this connection, it may be pointed out that it is possible to have two soaps of equal water content (as measured by the Fischer or even the Dean and Stark method), one of which will break down and the other remain satisfactory. In other words, the tolerance for water of different soap batches will vary, depending on the state of the water present, the amount of free acid content, etc.

IX. <u>Gel Additives to Eliminate Unburned Residue, Increase Density, etc.</u> The full heat of Napalm gels is not realized since these fuels do not burn to an ash when ejected from a flame thrower. The reason for this is obvious as the gels can be burnt completely to an ash if heated strongly enough in a plentiful supply of oxygen. These conditions can be realized if an oxygen supplying material is contained in the burning mass. The addition of a nitrate, a chlorate or a perchlorate in finely divided form immediately after the X-104-B has absorbed all the solvent accomplishes this purpose and, moreover, at the same time, increases the density of the fuel. Nitrates furnish the most oxygen per unit weight of additive, but do not necessarily supply the greatest number of calories per gram and the actual combustion is more vigorous with perchlorates. At the same time also, the flame intensity may be further increased by adding a non-organic combustible material to the gel. The following calculations of heats of combustion of non-organic substances show that boron has the largest heat of combustion, carbon next and aluminum third.

Relative Heats of Combustion of Fuel Additives

Combustible	Oxidizing Agent	Products	Calories evolved per gram of combustible
B	$KClO_3$	B_2O_3, KCl	13,800
C	$NaNO_3$	Na_2CO_3, N_2, CO_2	7,800
Al	$KClO_3$	Al_2O_3, KCl	7,590
Al	$NaClO_3$	$Al_2O_3, NaCl$	7,539
Al	$KClO_4$	Al_2O_3, KCl	7,180
Al	$NaClO_4$	$Al_2O_3, NaCl$	7,179
Al + C	$NaNO_3$	Al_2O_3, Na_2CO_3, N_2	6,610
Mg	$NaClO_4$	$MgO, NaCl$	5,980
Fe	$KClO_3$	Fe_3O_4, KCl	1,730
Fe	$KClO_4$	Fe_3O_4, KCl	1,560

Unfortunately, these figures give no indication of flame temperatures, which are actually more important with regard to complete combustion than are the heats of combustion themselves. In point of fact, it was found that the most vigorous combustion was obtained with a gel containing a mixture of aluminum dust and potassium perchlorate ground to 200 mesh. Mixtures containing amorphous boron, on the other hand, actually burned no better than one containing the oxidizing agent alone, considerable unburned boron being found in the residue.

The aluminum-perchlorate mixture was also found to be the most stable towards friction and shock, an important consideration. The most sensitive additive tried was red phosphorus with perchlorate, carbon and boron being intermediate in this respect. Phosphorus and sulfur, moreover, are not to be recommended as both produce strong acids when oxidized and may thus lead to gel breakdown, owing to metathesis with the soaps as a result of their acidic nature.

A combination of 2 grams of aluminum dust, 16 grams of potassium perchlorate and 100 grams of 8 per cent gel gives an improved mixture which burns completely to an ash but does not start burning vigorously until

CONFIDENTIAL

combustion of the gasoline is almost complete. In this way, the burning period is extended, and the total number of calories produced is increased. There is also a minor increase in density from 0.750 to 0.841. If the perchlorate is not sufficiently finely ground (to 200 mesh) it will settle from the suspension after a period of a week or less, depending on the degree of fineness. When the aluminum is replaced by magnesium, much spattering occurs and the heat transferred to the target is considerably reduced as a result.

X. Conclusion. Of the various questions studied in the course of the investigations described in the foregoing report, that of the prevention of oxidation of the aluminum soaps of the unsaturated fatty acids would appear to have the greatest practical significance. It has been shown conclusively that not only can this oxidation be prevented by the addition of various inhibitors but, also, that the presence of these compounds in the amounts necessary to be effective has no deleterious effect on gasoline gels containing the soaps in question. The addition of inhibitors in practice is simple and increases the cost of the finished product by a negligible amount. Moreover, it not only facilitates the manufacturing operation by lessening the strictness of control necessary, but ensures that the finished material will not deteriorate through oxidation in long periods of storage even under tropical conditions.

It would seem that further work might profitably be undertaken on the possibilities of various emulsions as, in this way, a completely combustible thickened fuel might be obtained, which, of course, is not possible when a soap is used as the thickening agent. The advantages of such a fuel might well be found to outweigh the disadvantage of the complication of equipment, which its preparation would involve. For this same reason, the preparation of gasoline gels by means of some readily and completely combustible gelling agent (as discussed on pages 4 and 5) should be further considered.

It is also considered, in view of the results already obtained, that the possibilities of tall oil soaps should be further investigated. This material is available in large quantities within the United States (in itself a point of no mean importance in view of the shipping situation) and very considerable economies would be effected by its substitution for part or all of the more expensive coconut and naphthenic acids, as these latter cost from twelve to fifteen cents per pounds as against four cents for the tall oil acids.

February 23, 1944
R[illegible]:mz

[illegible] Dawson

E. R. White

cc: 1 - E.P. Stevenson
1 - H.C. Hottel
4 - Dr. Johnstone
19 - R.H. Ewell

REEL - C

1344

A.T.I.

31601

~~CONFIDENTIAL~~

OVER

U

ATI-	31601
REVISION	(None)
ORIG. AGENCY NO.	(None)
PUBLISHING AGENCY NO.	OSRD-3506

TITLE: Flame Thrower Fuels

AUTHOR(S): Dawson, R. D.; White, E. R.
ORIGINATING AGENCY: Shell Development Co.
PUBLISHED BY: Office of Scientific Research and Development, NDRC, Div. 11

DATE	DOC. CLASS.	COUNTRY	LANGUAGE	PAGES	ILLUSTRATIONS
April '44	Confd'l	U.S.	Eng.	36	graphs, tables

ABSTRACT:

Investigation was made covering various methods of obtaining thickened fuels for use in flame throwers, the purpose of this thickening was to provide a fuel having a high calorific value, ready ignitability, adhesiveness, resistance to disintegration in flight, and stability in storage. Tests were made on thickened fuels obtained by suspensions of small particles of combustible solids in the fuel base, emulsions of gasoline with various liquids, and gasoline gels. The possible variations in the Napalm (aluminum soaps of coconut, naphthenic and oleic acids) formula, the effect of water and free acid, and soap complexity on gasoline gels are given. It was concluded that soaps made from cheaper and more readily obtainable sources of acid could be substituted for the standard Napalm acids.

DISTRIBUTION: Copies of this report obtainable from Air Documents Division; Attn: MCIDXD

DIVISION: ~~Ordnance and Armament (22)~~ 57
SECTION: ~~Chemicals and Incendiaries (11)~~ 5

SUBJECT HEADINGS: Flame throwers - Fortified fuels (37319.68)

B
2

ATI SHEET NO.: C-22-11-65

Air Documents Division, Intelligence Department
Air Materiel Command

AIR TECHNICAL INDEX

Wright-Patterson Air Force Base
Dayton, Ohio

~~CONFIDENTIAL~~

CLASSIFICATION CANCELLED
Ⓡ By authority OSRD List #3,
Dated 2-11 January 1946
By , USCO

18 SEP 1950

P 19/1/1

㉓

* Flamethrower fuels
Flamethrowers