FTD-HC-23-388-71

FOREIGN TECHNOLOGY DIVISION

AIR FORCE SYSTEMS COMMAND

CONSIDERATIONS REGARDING THE IMPROVEMENT OF THE QUALITIES OF MINERAL OILS WITH THE AID OF ADDITIVES

by

S. Ghita

FOREIGN TECHNOLOGY DIVISION

UNCLASSIFIED
Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Foreign Technology Division Air Force Systems Command U. S. Air Force	2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED 2b. GROUP

3. REPORT TITLE

CONSIDERATIONS REGARDING THE IMPROVEMENT OF THE QUALITIES OF MINERAL OILS WITH THE AID OF ADDITIVES

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

Translation

5. AUTHOR(S) (First name, middle initial, last name)

Ghita, S.

6. REPORT DATE November 1969	7a. TOTAL NO. OF PAGES 16	7b. NO. OF REFS 6
8a. CONTRACT OR GRANT NO. F33657-71-D-0057 b. PROJECT NO. 7343 c. d.	9a. ORIGINATOR'S REPORT NUMBER(S) FTD-HC-23-385-71 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	

10. DISTRIBUTION STATEMENT

Approved for public release; distribution unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Foreign Technology Division Wright-Patterson AFB, Ohio

13. ABSTRACT

Improvement in the design of internal combustion engines required to change the properties of oils used as fuel and lubricant is shown. The potential improvement of the properties of the lubricating oils by means of additives such as detergents, antioxidants, agents affecting the index of viscosity, depressants, anticongelation and anticorrosion agents and high pressure, high temperature additives was studied. These materials are added to the oil in a given range. The additives should have cumulative and polyfunctional properties. It is recommended to extend the use of multigrade oils in Roumania to satisfy the operation requirements of modern engines. [AP0118575]

DD FORM 1 NOV 65 1473

UNCLASSIFIED
Security Classification

UNCLASSIFIED

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Internal Combustion Engine						
Lubricating Oil						
Lubricant Additive						
Fuel Additive						
Detergent Additive						
Anticorrosion Additive						
Mineral Oil						

UNCLASSIFIED

Security Classification

EDITED TRANSLATION

CONSIDERATIONS REGARDING THE IMPROVEMENT OF THE QUALITIES OF MINERAL OILS WITH THE AID OF ADDITIVES

By: S. Ghita

English pages: 16

Source: Petrol si Gaze (Oil and Gas) 1969, Vol. 20, No. 11, pp. 622-626

Translated under: F33657-71-D-0057

RU/9004-69-020-011

THIS TRANSLATION IS A RENDITION OF THE ORIGINAL FOREIGN TEXT WITHOUT ANY ANALYTICAL OR EDITORIAL COMMENT. STATEMENTS OR THEORIES ADVOCATED OR IMPLIED ARE THOSE OF THE SOURCE AND DO NOT NECESSARILY REFLECT THE POSITION OR OPINION OF THE FOREIGN TECHNOLOGY DIVISION.	PREPARED BY: TRANSLATION DIVISION FOREIGN TECHNOLOGY DIVISION WP-AFB, OHIO.

CONSIDERATIONS REGARDING THE IMPROVEMENT OF THE QUALITIES OF MINERAL OILS WITH THE AID OF ADDITIVES

St. Ghita

The continuous development of our national economy leads to the growing demand for fuels and lubricants of motors and aggregates built on the concepts of modern technology.

Almost all machines, apparatus, and in general, actual complex mechanical constructions, whose number is growing rapidly, contain moving parts in which practical interest is increasing, and which require the development of knowledge and applications regarding friction and lubrication phenomena of contact surfaces.

There are more and more modern technical installations that cannot permit any temporary defects or interruptions of their functioning without grave consequences regarding their safety. The improvement of lubricant quality and the reduction of friction increase the productivity of the machine and the quality of the products produced, reduce the maintenance labor cost and repairs, and prolong the machine life, with the reduction of operational accidents [4].

Part of these problems were created by the evergrowing consumption of fuels and lubricants, the great number and diversity of engines and equipment, as well as the development of some types of engines with a high degree of compression (10:1 and 12:1) and with a braking power of 300 hp.

When two entirely different branches of science and technology met, such as the technology of crude oil and organic chemistry, on one hand, and mechanical engineering on the other, a new branch developed in the past 25 years — efficient utilization of fuels and lubricants for engines and aggregates.

*

The old Rumanian criteria for evaluating the quality of mineral oils only according to the viscosity indices do not correspond to actual demands. The new specifications refer to the detergency, oxidation, lubricating capacity, foaming, etc. In order to satisfy the above-mentioned conditions, some brand new products have been added to mineral oils, obtained by organic synthesis — utilizing for this, not only organic compounds, but also inorganic as well as organo-metallic compounds.

Utilizing additives for improving the quality of the oils became more and more necessary, because these could give oils the required supplementary qualities.

In countries with a well-developed industry, additives are used on a larger and larger scale, going as far as completely supplementing entire quantities of oils.

*

Additives are those substances which, when introduced in oils in small quantities of 2.10^{-4} - 12%, can give oils special qualities that they do not possess under normal conditions, or can preserve for a longer time certain qualities which would disappear with use.

To insure optimum lubrication, both for internal combustion engines and for certain mechanisms which function under more severe conditions, an oil has to meet certain conditions, among them the following:

— to resist oxidation phenomena better and to form as few acidic substances as possible;
— to form a resistant, oil film on the whole assembly of moving parts, to protect them as much as possible at high temperatures;
— to have a low congealing point and not too high a viscosity at low temperatures;
— to have a smaller variation of viscosity with temperature;
— not to produce corrosion of the gears which are very sensitive to the acidic products which are created by oil oxidation;
— to have detergent action.

The most representative additives which are needed to improve the qualities of oils, for lubricating internal combustion engines are:

— detergent and anti-oxidant additives;
— additives to improve the viscosity index;
— depressants (antifreezing agents) and anticorrosive additives;
— extreme pressure additives.

Without making a detailed analysis of the lubrication, it can be stated that this quality is conditioned by the adsorption phenomenon, the orientation of molecules on the contact surface of the moving parts.

According to some authors, the lubricating (greasing) effect is conditioned almost entirely by the mono-molecular layer. The essential difference appears between the first layer of adsorbed molecules, connected directly to the surface of the solid body, and the following molecules of the limiting layer.

When the contact pressure and temperature reach maximum values, the limiting layer "breaks", and dry friction appears.

Such a contact pressure does not develop uniformly over the entire surface of the body. On the other hand, simultaneously with the temperature rise to a value close to the fusion point of the additive with the metal, a sudden jump of the friction and wear occurs, under the conditions of mono-nuclear lubrication.

The interaction energy of the additives with the metals or even with the metallic oxide does not limit the effectiveness of the additives. In many cases, physical adsorption and bonding with hydrogen insures a permanent contact between the additive and the surface of the metal.

During the engine operation, the additive action decreases according to a linear law. The mineral oils in contact with the warm metal form carbonic compounds which are deposited on the surface of the metal as a fine resistant layer, which are called lacquers.

The sediments of lacquers represent the products of hydrocarbon oxidation, and the speed of the formation depends on a series of factors, such as: warming temperature, the catalytic action of the metal, the type of contact of the hydrocarbon surface (liquid or vapor), as well as their chemical composition. The composition of the lacquers could include the following products: the initial product, resins, hydroxy acids, asphaltenes, carbenes, and carboids.

The oxidation products of hydrocarbons such as: the resins, hydroxy acids, and asphaltenes, are more active than the hydrocarbon, and as the oxidation process of the marginal layer of the oils proceeds, they will be retained more strongly on the surface than the adsorbed molecules. After 50 hours of oil use in the engine, the contents of aldehyde could reach approximately 10% of the entire quantity of carbonyl compounds.

The ketones are the basic products of carbonyl compounds, which are formed as a result of decomposition of the hydroperoxides. The ketone content could reach 80% of the entire quantity of the carbonyl compounds formed.

From the naphthene-paraffin hydrocarbons, twice as many ketones are formed than from the polycyclic aromatic hydrocarbons: the monocyclic aromatic hydrocarbons occupy an intermediary position.

To improve the lubrication properties of engine oils, two types of additives are simultaneously added, usually detergents and antioxidants. In the majority of cases, as detergent additives, sulpnonates, and calcium and barium alkylphenolates are used.

The purpose of the second type of additive is to improve the antioxidant, anticorrosive, and anti-wear qualities. As for the second type of additives, usually organic compounds with phosphorus content are used, to increase the resistance of the lubricating film.

For the oils used at Diesel engine lubrications, which function under more severe conditions (higher temperatures), the products of the reaction between phosphorus pentasulphide and unsaturated hydrocarbons (terepenes and polyolefin) [2,5] are used.

*

Presently, the additives used on a large scale are the acid ester salts of dialkyldithiophosphoric acid (dialkyldithiophosphates) of $(RO)_2 - PSS - M_2 - PSS - (OR)_2$ structure, which are multifunctional additives, intended for motor and equipment lubrication. These additives have detergent, anticorrosive, and anti-wear qualities, and in addition to the above they are antioxidants, depressants, and deemulsification agents. The properties of the dialkyldithiophosphates depend on their chemical structure.

The metallic dialkyldithiophosphates (the additives of the type listed below) are synthesized by starting from technical alcohols. From the interaction of the alcohols with phosphorus pentasulphide, acid esters are obtained of dithiophosphoric acid which then become the salts of the respective metal [5].

THE CHEMICAL STRUCTURE OF THE DIALKYLDITHIOPHOSPHATE ADDITIVES

No.	Additive	Formula
1	"	$[(RO)_2 - PSS]_2Ba \quad R = C_{20} - C_{24}$
2	"	$[(RO)_2 - PSS]_2Ba \quad R = C_{16} - C_{20}$
3	"	$[(CH_3)(CH_2)]_2 - CH_2O)_2PSS]_2Ba$
4	"	$[(RO)_2 - PSS]_2 - Zn \quad R = C_{20} - C_{24}$
5	"	$[(CH_3(CH_2)_4 CHO)_2 - PSS]_2Zn$ | CH_3
6	"	$[(CH_3-(CH_2)_3-CH-(CH_2O)_2-PSS]_2-Zn$ | C_2H_5
7	"	$[(CH_3-(CH_2)_3-(COH)_2] - PSS-Zn-PSS$ | CH_3 $[OCH_2 - CH - (CH_3)_2]_2$
8	"	$[CH_3 - (CH_2)_3 - CH - CHO]_2-PSS-Zn$ | C_2H_5 $-PSS-[(OCH_2 - CH(CH_3)_2]_2.$

Number 1, 2, and 3 additives represent the barium dialkyldithiophosphates, and the rest are zinc dialkyldithiophosphates.

To obtain No. 1 and 4 additives, technical alcohols with heavy molecular weight are used, which are obtained by direct oxidation of the paraffin fractions. The alcohols obtained by the oxidation of the synthetic paraffin fraction have a boiling point between 270 and 320° C. The molecular weight of the alcohols corresponds to C_{16} - C_{20} and C_{20} - C_{24}. No. 5 additives are obtained on the basis of secondary octyl alcohol, and No. [illegible] additives — by using primary octyl alcohol, which in industry is known as the ipooctyl alcohol

No. 7 and 8 additives were obtained from isooctyl alcohol and octyl alcohol, and contain radicals with different structures. To obtain additive No. 7, iscbutyl alcohol and secondary octyl alcohols are used, and for additive No. 8, isobutyl and isooctyl alcohols are used.

The properties of dialkyldithiophosphates, and especially their influence on the conditions of oil use, depend on the value and the structure of the radical. For example, dithiophosphoric additives, synthesized on the basis of alcohols with heavy molecular weight, have good anticorrosive and antioxidant properties, and, at the same time, they have depressant qualities.

The additives made on the basis of alcohols with light molecular structure do not have depressant qualities. According to some authors, when using zinc dialkyldithiophosphates (anticorrosive and detergent additives), the ability of the additives to improve quality is diminished as the molecular weight of the component is reduced, that is, reducing the value of the radical.

*

Depressant Detergent Additives

As was shown before, simultaneously with the oxidation phenomena, substances with heavy molecular structure are formed, such as: resins, asphaltenes, and carbenes which are insoluble in oil and could form resistant lacquers on the warm parts of the engine, in some cases blocking the compression rings.

The term detergent additive has wide usage, because their action is similar to the commonly known detergent substances (soaps, sulphonates, salts of organic acids, etc.).

In many cases, the detergent effectiveness of the additives is analyzed in terms of the relative cleanliness of the most important part of the engine. The formation of insoluble oxidation products in oil is due to the influence of fuel composition, lubricating oil, and operational conditions of the engine, etc. Some of the conditions under which engines operate that favor the appearance of insoluble substances in the oil, are the following: the technical regime of the engine, the catalytic influence of the metals — for example, iron and copper, which yield the respective halides — the presence of water in the crank case, etc.

Oils without additives do not possess sufficient properties to prevent insoluble precipitation during engine operation.

To avoid these phenomena, it is recommended that detergent additives be added to oil which will give them entirely new properties.

Works in this field mention that a great number of different organic substances were suggested as detergent additives.

It has also been ascertained that any attempt to correlate the structure of the suggested detergent substances and their action is very hard to establish.

This can also be seen from the fact that, for this category of additives, substances having different compositions and structure were proposed.

The most representative classes are:

- the metallic salts of sulphonic derivatives of hydrocarbons;
- the metallic salts of the naphthalic acids;
- the metallic salts of fatty acids;
- organic esters with very varied structures;
- organo-phosphoric esters and their derivatives;
- sulphides and free phenolic polysulphides or barium salts;
- disubstituted, dithiophosphoric acids.

The fundamental property of detergent additives is their capacity to disperse insoluble products of condensation and incomplete combustion, and to stabilize their suspension in the oil. The detergent additives, as superficially active substances, are absorbed on the insoluble particles formed in oil, thus preventing their precipitation on parts of the engine [5].

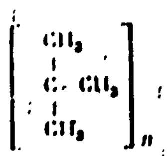
Additives for Improving the Viscosity Index

Very few mineral oils satisfy the viscosity-temperature conditions, or in other words, have sufficient viscosity at high temperatures and remain fluid at low temperatures.

To give oil satisfactory qualities, it is absolutely necessary to add to them different quantities of additives which will increase the viscosity index.

The utilization on a large scale in the industrialized countries of multigrade oils leads to the growing importance of additives for improving the viscosity index. Studies and research for the past 20 - 25 years have brought to light the valuable properties of additives on the basis of macromolecules, to increase the viscosity index. The types of polymers used as additives for improving the viscosity index and the agents for lowering the freezing point are:

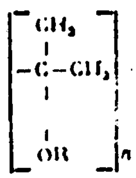
— polyisobutylenes
— polymethacrylates
— alkylate polystyrenes
— the polymers of vinyl esters.



Polyisobutylene was the first polymer used as an additive to improve the viscosity index. Initially it was used only for lowering the freezing point.

Since polyisobutylene is a linearly saturated compound, it is resistant to the action of oxygen, resists the effects of a temperature of about 300° C without suffering any depolymerization, conserving its rheologic properties during the time it is used.

In equal concentrations, the viscosity index of an oil increases as the molecular weight of the polymer increases. Another factor, just as important, consists of the nature of the basic oil. The effect of the polymer thickening, and thus an increase in the viscosity index, is more pronounced for oils of a naphthenic nature than those of a paraffin nature, having the same viscosity.



The polymethacrylates are the most widely utilized additives for improving the viscosity index and lowering the freezing point, and simultaneously having the property of a stabilizer.

The most frequently used esters are:

— n-butyl polymethacrylates
— n-heptylpolymethacrylates
— lauryl, cetyl, and octodecyl polymethacrylates.

The inferior polymers are liquids, while the superior ones are hard and opaque waxes. Their solubility in oils and hydrocarbons increases with the molecular weight of the substitute R.

Polymethacrylate is stable at the working temperature of oil in engines. The resistance of polymethacrylate to oxidation is good. Thus it has an inhibiting property, protecting the oil. Polymethacrylate which is used as an additive has, in general, a molecular weight on the order of 5000 - 20,000, with a high viscosity index. They are superior to the polyisobutylenes, and at equal concentrations lead to a greater increase of the viscosity index.

Depressant (Antifreeze) Additives

One of the basic properties that is demanded of an oil is to maintain its fluidity at low temperatures — a quality which insures better engine lubrication. The paraffin oils naturally possess good lubricating properties, but have a high congealing point.

The congealing point of a paraffin oil can be defined as the temperature at which the crystallization of the paraffins takes place and thus, the oil ceases to flow.

Oils with low congealing points can be obtained from paraffin raw materials in two ways:

a) by dewaxing (paraffin removal) at very low temperature. This is quite a disadvantageous operation, because by removing the long chains of the paraffins, its viscosity index (I.V.) as well as its resistance to oxidation decrease;

b) partial dewaxing and addition of an anti-freezing agent. The antifreeze additives are surface active substances which lower the congealing temperature and maintain the fluidity of the oils at low temperature, decreasing the engine wear in cold seasons.

The natural anti-freeze agents include asphalt substances which have the disadvantage of possessing a low effectiveness. There are other chemical substances which have an antifreeze effect on some oils, for example: benzoyl chloride, aluminum stearate, cholesterol esters, and oxidized vinyl compounds. These substances have the disadvantage of a complicated and expensive technology process needed to produce them.

There are several theories showing how an antifreeze agent acts on the mineral oils. Some of them explain mechanisms of this action in two ways:

a) by creating the conditions for enlarging the crystals which make possible a greater mobility. In this case, the action occurs in a volume, where the particles of the antifreeze additives constitute crystallization centers aroung which paraffin crystals gather in a compact form.

b) by creating eutectic mixtures formed of antifreeze agents and paraffin with a low melting point, solvent in the liquid phase, which decreases the quantity and size of the crystals. This way, surface action takes place, preventing the formation of a crystal lattice, and allowing the free flow of the oil.

Among the substances with depressant properties are paraflow and santopor substances.

The paraflow acts especially on paraffins with a low melting point. The antifreeze agents with high surface action act best on components which crystallize more readily in oil, that is, on paraffins with high melting point.

The santopor maintains the paraffins with low melting temperature in solution, and those with high melting point from agglomerates which precipitate, influencing the oil fluidity.

The action of the antifreezing agents is a function of the following:

— crystal structure
— structural modifications of paraffins
— the equilibrium transition state from solid to liquid phase, which is caused, in both cases, by the presence of paraffin substances.

Additives for Extreme Pressure (High Temperature)

The high speeds and pressures that are encountered in some machines and equipment, especially in hypoid gears, provided the impetus for research to obtain lubricants with adequate qualities.

The chemical nature of a lubricant used at very high pressures was the object of numerous studies, which led to the conclusion that chemical reactions with lubricant surfaces are favored by high pressure, and additives with good antifreezing properties are adsorbed by friction surfaces. The compounds resulting from the chemical reactions have a favorable influence on the working conditions, not only because they reduce the roughness, but also because they fill the gap between irregularities.

The temperature constitutes an important factor in evaluating oils which are used under severe operational conditions (extreme pressure). It is even more important than pressure, and there are proposals to call them additives "for high temperature".

To understand the mechanism of extreme pressure additives, we must show how complex organic compounds of the trialkyl phosphate type can form (under high pressure and temperature conditions) relatively simple compounds (metallic phosphides) which are adsorbed on the metallic surfaces of the oleaginous solution.

Under conditions of maximum stress, at the contact points temperatures develop that surpass the thermal stability of the trialkyl phosphates. These decompose, forming simple compounds which interact with the metal (phosphide and the respective sulphides of the metals).

A common characteristic of all types of additives which contain organic compounds, such as Cl, S, P, as well as the phosphororganic compounds, is that at high temperatures and pressure, they undergo chemical transformation and form relatively simple compounds, which are adsorbed on the surface of the metal, reducing the roughness [6].

During decomposition, oxidation and reduction reactions occur simultaneously with the formation of phosphoric acid and phosphorine:

$$4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$$

Additives for Multigrade Oils

The multigrade oils satisfy the viscosity conditions which are demanded for two or more qualities (grades). They may thus be used for different engines, for cold as well as for hot seasons.

Use of multigrade oils for engine lubrication is also necessary, because they have high fluidity at low temperatures and sufficient viscosity at high temperatures, thus permitting an easy start and insuring optimum lubrication of the moving parts.

These oils have to correspond to severe operational conditions. For this reason, when producing multigrade oils, oil fractions with a lower viscosity are used to which sufficient additives are added to raise its viscosity index to about 140.

To obtain a multigrade oil of about 8% polymer, 6% detergent, and 1.5% oxidation inhibitors, etc., are used.

Conclusions

From examining the mechanism of the additive action, we find that to insure good operation of engines and equipment which work under changing conditions of high temperatures and pressures, they must be lubricated with high quality oils (additives added to them).

The most representative additives are detergent, antioxidant, anticorrosive, and additives to improve the viscosity index, lubricating capacity, antifreezing properties, etc. Their proportion in oil can vary from $2 \cdot 10^{-4}$ and 12%. This is a function of the nature of the raw material, the place, and the conditions under which it is used.

It has to be taken into consideration that the properties of these additives should build up and to have polyfunctional qualities their actions must supplement each other and be mutually complementary as much as possible.

Utilizing polyfunctional additives to improve the quality of mineral oil is becoming more and more necessary, and it is used more and more, because use of the most favorable raw materials and the application of the most modern manufacturing technology to obtain mineral oils do not lead to products which totally satisfy the functional demands of engines and mechanisms that function under severe conditions.

Expansion of multigrade oils is being done in our country as well, because their physico-chemical characteristics satisfy the conditions imposed by the operation of modern engines, leading at the same time to important savings of mineral oils

REFERENCES

1. Aramă, C. ş. a.: Combustibili şi lubrifianţi pentru motoare. Editura tehnică, Bucureşti, 1962.
2. Papoc, K. K. Mecanismul acţiunii aditivilor detergenţi şi antioxidanţi la formarea lacurilor, p. 185.
3. Rădulescu, S. A. Aditivi pentru produse petroliere. În: Petrol şi Gaze, 7, nr. 8/1955, p. 312, 384.
4. Larson, R. Scient. Lubricat, 10, nr. 2, 1958, p. 12.
5. Rădulescu, S. A. Tehnologia uleiurilor minerale. Ed. tehnică, Bucureşti, 1958.
6. Smalheer, C. V. In: Chemical Additives for Gypold Gvarom, nr. 57, 1957.