

UNITED STATES PATENT OFFICE

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DIESEL ENGINE FUEL

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7 Claims. (Cl. 44—57)

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This invention relates to improved compression ignition engine fuels and is concerned primarily with the improvement of the ignition characteristics of fuels of this type. More particularly this invention relates to the improvement in the ignition qualities of untreated or pretreated Diesel fuels obtained by the addition to such fuels of ignition accelerators.

It is well known that in the operation of high speed compression ignition engines, such as Diesel engines, the ease in starting and the smoothness of running depends largely on the ignition quality of the fuel. This is determined by the interval of time required to initiate burning, known as the ignition delay period, and is concerned primarily in the heating of the surface material of the droplets of the fuel within the cylinder to a temperature at which combustion is initiated. The more favorable the ignition quality of the fuel, generally related to the paraffinicity thereof, the shorter will be the period of ignition delay. During the second stage of the combustion cycle the fuel that has accumulated in the combustion space burns causing a rapid increase in pressure, which increase is a function of the amount of fuel accumulated and as a consequence if the ignition delay period is sufficiently long to allow an excessive accumulation of fuel the sudden increase in pressure will be sufficient to cause detonation. While this characteristic of fuel is fundamentally determined by ignition lag measured by the degree of crank angle between injection and combustion of the fuel it is appropriately and conveniently measured by an arbitrary value or cetane number which is the per cent by volume of normal cetane in a mixture of normal cetane and alpha-methyl naphthalene having an ignition lag equivalent to that of the fuel being rated. On this basis the cetane number is related to the interval between the instant of full injection and the instant of ignition of the fuel in the combustion chamber of the engine and the shorter the ignition delay period the higher the cetane number. The concept of cetane value and the method for its determination are described and defined on page 172 of the 1943 issue of the A. S. T. M. Standards on Petroleum Products and Lubricants prepared by the A. S. T. M. Committee D-2 on Petroleum Products and Lubricants.

Ordinary high quality Diesel fuel has a cetane number of 40-47 and it is desirable in many instances to increase this value to 50-55 or even higher. It is known that by means of special refining processes such as extraction of ordinary distilled fuel with sulfur dioxide, heavy acid treatment with sulfuric acid, or the like, it is possible to increase the cetane number of the fuel by removing in the first instance aromatic hydrocarbons and by acid treatment removing the unsaturated hydrocarbons in either case increasing

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the relative paraffinicity of the fuel. However, such treatments are usually costly and wasteful of fuel due to the relatively high treating losses for a given increase in cetane number.

Diesel fuels, as ordinarily employed in compression ignition engines are petroleum hydrocarbon fractions having A. S. T. M. boiling ranges of from about 400° F. to about 700° F. but in certain cases special Diesel fuels are prepared which may exhibit initial boiling points as low as about 300° F. or final boiling points as high as about 800° F. when extrapolated to atmospheric pressure. As hereinbefore mentioned these fuels may be treated in various ways to remove certain of the less desirable constituents therefrom or they may be employed without pretreatment as obtained directly from the fractionating columns. It is to be understood that any and all of these fuels, regardless of boiling range composition or type of pretreatment, which may be employed in a compression-combustion engine fall within the definition of Diesel fuels according to this invention.

Much work has been done to discover a method for treating Diesel fuels to reduce ignition delay and to increase the ease of starting. One of the major fields of investigation has been the development of compounds known as ignition accelerators which may be added to Diesel fuels in comparatively small amounts to impart thereto higher cetane values. For example peroxides, nitrates of glycerols, nitrates of glycols, and several low molecular weight alkyl nitrates and nitrites are among the proposed compounds. It is thought that these substances may function as intermediates in the combustion chamber igniting therein at a temperature below that of the Diesel fuel to which they are added, and thereby accelerating the ignition of the Diesel fuel within the chamber. For simplicity this action may be characterized by the material on a match head which by igniting at low temperatures brings about the ignition of the wood. As yet there has been no definite correlation between the cetane number of a fuel and its cold starting characteristics. By cold starting properties of a fuel is meant the minimum temperature at which a compression ignition engine fuel will ignite at a given compression ratio and determines under what condition such a fuel may be employed in starting a Diesel type engine. Whereas, in general the fuels of higher cetane number are found to have lower cold starting temperatures, this is not always true particularly in those cases where the cetane number has been increased by the addition of certain ignition accelerators. For example, it has been found that upon the addition to a Diesel fuel of a small quantity of amyl nitrate the decrease in cold starting temperature is proportional to the increase in cetane number, but with further addition of amyl nitrate, whereas

the cetane number is proportionately further increased, it is found that the cold starting temperature increases rather than decreases. On the other hand, upon the addition of peroxide type additives, and particularly hydrocarbon peroxides, the cold starting temperature decreases in proportion to the increase in cetane number over a comparatively wide range of peroxide concentration. It is clearly evident that such a characteristic as exhibited by the peroxide constitutes a big factor in its favor over the use of such compounds as the amyl nitrate which as pointed out above, does not correspondingly improve the cold starting characteristics of the fuels to which they are added.

On the other hand certain of the ignition accelerators hereinbefore employed have the tendency to catalyze the formation of gums in Diesel fuels to which they are added. Such gum formation is obviously undesirable because of its effect in the cylinders and fuel injectors of the motors.

It is an object of my invention therefore to improve the operation of compression ignition engines by the introduction of an ignition accelerator into the combustion chamber of said engine.

It is a further object of this invention to prepare an improved Diesel fuel by the addition thereto of an ignition accelerator of the type hereinafter disclosed.

It is a more particular object of my invention to prepare a Diesel engine fuel having improved ignition properties and low gum forming tendencies by the addition thereto of the ignition accelerators of this invention.

It is another object of my invention to treat a sulfur containing Diesel fuel so as to improve its performance in a compression ignition engine which treatment does not involve the removal of the sulfur containing compounds from said fuel.

Other objects and advantages of my invention will become apparent to those skilled in the art as the description thereof proceeds.

I have discovered that certain oxygenated or oxidized sulfur compounds such as sulfoxides and sulfones, and particularly sulfoxides, when added to a Diesel fuel in relatively minor amounts have the effect of materially increasing the cetane value of said fuel.

I am fully aware that the detrimental effect of certain sulfur containing hydrocarbons on the ignition properties of Diesel fuels has been appreciated by investigators in this field and that considerable work has been done toward removing such sulfur containing compounds or conversion of certain of said compounds such as for example mercaptans to disulfides which are found to exercise certain ignition accelerating properties in themselves. However, as the description of my invention proceeds it will become apparent that such is not the purpose thereof inasmuch as I have definitely established that the oxidized sulfur containing compounds and in particular the sulfoxides are excellent ignition accelerators and that said sulfoxides may not only be formed within a sulfur containing fuel, but may be added in relatively pure form to a sulfur free fuel wherein, in either case, an increase in cetane value of the fuel is realized.

In Table I below is given the results of the addition of only a few of these sulfoxides to a straight run sulfur free Diesel fuel having a cetane number of 48.5. Included in this table are the values for the gum formation within said

fuel before and after addition of the various sulfoxides.

The gum values as given in Table I were determined as follows: One hundred ml. of the Diesel fuel to be tested was placed in a Pyrex evaporating dish and maintained therein at 100° C. for a period of 16 hours. After the high temperature storage, employed to accelerate the gum formation, the samples were allowed to stand at room temperature for five hours to cool and to allow time for the last traces of the gum to settle. The Diesel fuel was then poured out of the evaporating dish which was allowed to drain for a period of one half hour, rinsed twice with a light hydrocarbon fraction such as a fraction boiling between 100° F. and 200° F., to remove the last traces of the heavier fuel, allowed to dry for one half hour and weighed. The precipitated gums, determined by the increase in weight of the evaporating dish, are recorded as milligrams of gum for 100 ml. of fuel.

TABLE I

Effect of various sulfoxides on the cetane number of a straight run Diesel fuel

Addition	Per Cent	Cetane Number	Gum	Corrosion
None.....		48.5	5	Pass.
Butyl sulfoxide.....	1	53	3	Do.
Do.....	2	55	5	Do.
Ethyl sulfoxide.....	1	52	3	Do.
Do.....	2	52.5	5	Do.
Methyl sulfoxide.....	1	51	5	Do.

The cetane values given herein were determined by the critical compression method of evaluation. However, cetane values may also be determined by the C. F. R. method (delay method). Both of these methods give the same results on an undoped Diesel fuel, i. e. free from added ignition accelerators but the C. F. R. method, which has become the official test, shows almost twice the cetane increase in doped fuel than the critical compression values. The cetane values given throughout this disclosure were determined by the critical compression method of evaluation giving values on the fuels to which the sulfoxides had been added lower than would a determination by the C. F. R. method.

It is interesting to note the effect of butyl sulfide alone and after oxidation with hydrogen peroxide and dimethylcyclopentane peroxide on a catalytically cracked gas oil. These data together with the cetane value of the original stock are shown in Table II.

TABLE II

Addition	Per cent by weight	Per cent Peroxide	Cetane Number		
			Straight run Diesel	Catalytically Cracked Gas Oil	X Diesel
None.....		0	48.5	35.5	36.0
N-butyl sulfide.....	2.2	0	50.0	37.0	37.5
Product from n-Bu ₂ S+H ₂ O ₂	2.0	0	51.5	41.5	41.0
Product from n-Bu ₂ S+ D. M. P. O. Peroxide.....	2.2	0.27	53.5	42.5	42.0

It is seen that although the n-butyl sulfide has a small beneficial effect on the cetane number it is not comparable to that obtained upon oxidation of the sulfide to a sulfoxide, the 0.27% per-

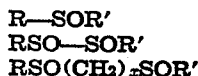
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oxide remaining after oxidation of the butyl sulfide being insufficient to account for any appreciable cetane number increase.

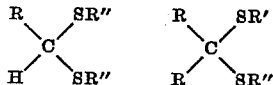
It is apparent from the results of Table I above that the sulfoxides in improving the cetane number of the fuel do not in any way increase the gum formation within said fuel contrary to what is found with certain other ignition accelerators.

It is to be understood that these examples do not limit my invention to the use of those sulfoxides shown inasmuch as I have found that sulfoxides derived from a large variety of compounds are excellent ignition accelerators.

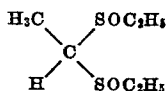
For example the sulfoxides to be used according to my invention may be derived from the alkyl sulfides or polysulfides as hereinbefore disclosed including such compounds as ethyl sulfoxide, butyl sulfoxide, amyl sulfoxide, dimethyl disulfoxide, methyl ethyl sulfoxide, diethyl disulfoxide, ethyl amyl sulfoxide, ethyl iso-amyl sulfoxide, trimethylene-bis-methyl-sulfoxide, trimethylene-bis-ethyl sulfoxide, and the like, such compounds having the general formulas



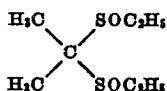
in which R and R' may be alkyl, cycloalkyl, aryl or aralkyl groups which would include such compounds not only as listed above in which R and R' were both alkyl groups but phenyl methyl sulfoxide, phenyl ethyl sulfoxide, phenyl ethyl disulfoxide, methyl benzyl sulfoxide, and the like, or the sulfoxides may be derived from the mercaptals or mercaptols which compounds have the empirical formulas



in which R, R' and R'' represent hydrocarbon radicals such as those hereinbefore mentioned which may be the same or different from each other. The mercaptals are formed by the interaction of one molecule of an aldehyde and two molecules of a mercaptan and the sulfoxides derived therefrom may be represented for example by α -bis-ethyl-sulfinyl-ethane



derived from acetaldehyde-mercaptopal. The mercaptols are formed by the interaction of one molecule of a ketone and two molecules of mercaptan and the sulfoxides derived therefrom may be represented for example by $\beta\beta$ -bis-ethyl-sulfinyl-propane



derived from acetone mercaptol, or mercaptols from diketones as for example $\beta\beta, \alpha\alpha$ -Tetrakis ethyl-sulfinyl hexane



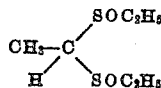
Further the sulfoxides may be prepared by the interaction of sulfur dioxide with hydrocarbons, mercaptans or other substituted hydrocarbons or by the interaction of thionyl chloride and hydrocarbons. In general the oxidized sulfur compounds which I may employ, with the exception

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of the cyclic sulfur compounds which will be discussed hereinafter, may be represented by the empirical formula



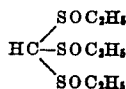
in which n is preferably equal to one but may be two and m is equal to one, two, three or higher. R is an alkyl, cycloalkyl, aralkyl or aryl group and R' is an alkyl, aralkyl or aryl group which may be interrupted by O, S, SO, SO₂ or substituted by these groups. Thus in the compound



n will equal 1, m will equal 1, R will correspond to C₂H₅ and R' will encompass CH₃-C-SO C₂H₅ being an alkyl group interrupted by an SO group. In this manner the sulfoxides prepared from various organic compounds such as for example the ortho thio esters having the general formula

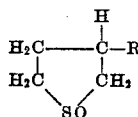


may be represented such as for example the sulfoxide of triethyl trithio ortho-formate

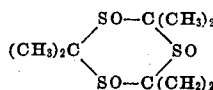


and the like.

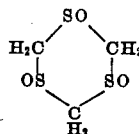
The cyclic sulfur compounds may also be oxidized to form sulfoxides or sulfones which I have found to be excellent ignition accelerators when added to Diesel fuels. Compounds of this nature include the cyclic compounds containing one or more sulfur atoms in the ring. For example thiophanes or alkyl thiophanes may be readily oxidized to give compounds such as



in which R represents any alkylating group and may be attached to any carbon atoms in the ring. In addition to the more common thiophane type compounds I may employ the cyclic sulfoxides having 3, 4 and 6 atoms in the ring or sulfoxides having more than one SO groupage in the ring such as for example trithio acetone sulfoxide.



or the sulfoxide of trithiane



and the like.

As an example of the usage of sulfoxides prepared from the heterocyclic sulfur compounds a concentrate of a mixture of alkyl thiophanes was separated from a sulfur rich petroleum fraction which mixture boiled at about 300° F. This concentrate analyzed 20 per cent sulfur and on the basis of calculations had an average structure of 9 carbon atoms indicating the presence of five

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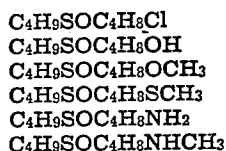
carbon atoms attached to the thiophane nucleus. This material was treated with dimethylcyclopentane peroxides to convert the sulfur to the sulfoxide and was subsequently added to a straight run diesel with the following results.

TABLE III

Addition	Per cent by Weight	Peroxide in fuel, per cent	Cetane Number
None		0	48.5
Thiophanes (see above)	2.2	0	48.5
Product from thiophanes and dimethylcyclopentane peroxide	2.2	.16	52.5

It is apparent that the thiophane sulfoxide, present in the fuel to the extent of about 2 per cent was responsible for the increase of about 4 in the cetane number of the fuel determined by the critical compression method inasmuch as the 0.16 per cent of dimethylcyclopentane peroxide present would be insufficient to cause any appreciable change in the cetane value.

Besides the sulfoxides mentioned herein, substituted derivatives of the sulfoxides containing the groups OR, SR, X, NR' R where R and R' represent hydrogen or a hydrocarbon radical and X represents a halogen, may also be used. Examples of such compounds are the derivatives of dibutyl sulfoxide $C_4H_9SOC_4H_9$ such as:

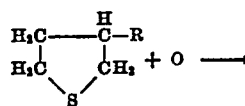


Other methods of preparation of the sulfoxides or derivatives thereof may occur to those skilled in the art without departing from the scope of this invention inasmuch as the invention does not reside in the preparation of the sulfoxides or sulfones but in the utilization of these compounds as ignition accelerators for compression-combustion engine fuels.

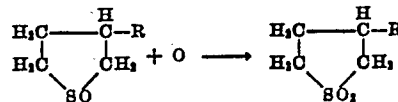
I may for example prepare sulfoxides in a Diesel fuel in situ either by addition of a suitable sulfur compound to a sulfur free fuel with subsequent oxidation therein to the sulfoxides and sulfones, or by addition of such compound to a Diesel fuel already contaminated with a small percentage of sulfur compounds wherein upon oxidation those sulfur containing compounds already present in the fuel will be oxidized together with the added sulfur compounds, the latter being employed in any desired quantity depending on the amount of sulfoxides desired in the treated fuel and upon the proportion of the desired amount satisfied by the oxidation of the sulfur compounds originally present in the fuel. In certain sections of the country Diesel fuels may be prepared having a sufficiently high sulfur content to give, upon oxidation, the desired percentage of sulfoxides in which case the addition of added amounts of sulfur compounds as above described is unnecessary.

The reaction which may take place within the fuel can be simply represented by the conversion of an organic sulfur containing compound to a sulfoxide or sulfone. It is believed that the alkylated thiophanes and alkyl sulfides are the sulfur containing compounds in Diesel fuels which react with oxidizing agents to form sulfoxides or sulfones, which reactions may be represented by the oxidation of thiophane as follows:

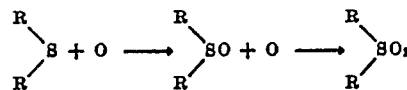
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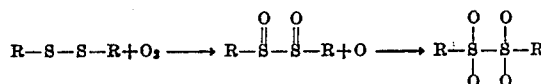
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10 and the oxidation of alkyl sulfides or polysulfides



15 and



20 in which R in any of the above compounds may consist of any substituted or unsubstituted hydrocarbon groupage containing from 2 to 20 carbon atoms. It is to be stressed that on the basis of data hereinafter set forth it is apparent that in the oxidation of the sulfur containing compounds in a Diesel fuel the predominate reaction is the formation of the sulfoxides and not the sulfones.

The conversion of said sulfur compounds within a Diesel fuel whether originally present therein or added thereto may be accomplished by any desirable oxidizing agent such as a peroxide, perchlorate, nitric acid, chlorine, bromine or chlorine dioxide, hypochlorous, chlorous or chloric acid, or their salts, chromic acid or chromates, selenium dioxide, potassium permanganate, and other well known oxidizing agents. For example, 100 volumes of a 47 cetane number Diesel fuel containing 0.7% sulfur in the form of various sulfur compounds was agitated for two hours with 50 volumes of 5% sodium hypochlorite solution after which the sodium hypochlorite solution was separated from the fuel, which fuel upon analysis showed no change in sulfur content but did exhibit a cetane value of 51 representing an increase of 4.

It is my belief that the beneficial effect of the oxidized sulfur compounds, and particularly of the sulfoxides, is due to their decomposition in the combustion chamber of the compression-ignition engine to liberate oxygen thus initiating the oxidation and combustion of the fuel. On the basis of this proposed mechanism I am able to explain the superiority of the sulfoxides over the sulfones for this purpose. Although the sulfones may be employed according to my invention, I have found that the sulfoxides are superior additives presumably, if the above hypothesis is correct, because of their relative instability as compared to the sulfones. The sulfinyl or sulfoxide groupage $S=O$ apparently when present in any compound will when added to a Diesel fuel become an ignition accelerator the compound liberating oxygen as described above. The sulfone or sulfonyl groupage



70 is however considerably more stable than the sulfoxide and as a consequence is an inferior ignition accelerator. Although my invention includes the usage of any of the compounds containing the sulfinyl groupage it is to be pointed out that certain of these compounds are more

effective than others due presumably to their relative stabilities.

The methods of application and use of these sulfoxides may be many and varied. As for example, as described above, the sulfoxides may be incorporated in a Diesel fuel by the oxidation of the sulfur compounds within or added to the Diesel fuel in which case sulfoxides, and sulfones will result. This oxidation may be carried out in a number of ways depending upon the oxidizing agent employed. In any case the reaction may be carried out at normal temperatures and pressures by agitation of the fuel to which the oxidizing agent has been added. If an aqueous solution of an oxidizing agent is employed the solution after agitation may be readily separated from the treated Diesel fuel by settling. In some cases the sulfoxides formed may be soluble in such solutions which property is utilized as hereinafter described to obtain sulfoxides from sulfur rich petroleum fractions. Other oxidizing agents, as for example the peroxides, may be readily dissolved in the fuel wherein the oxidation of the sulfur compounds is effected at the expense of a decomposition of the oxidizing agent eliminating the necessity of any subsequent separation procedure.

It also may be desirable to prepare the desired compounds by oxidizing the sulfur compounds in a sulfur rich oil such as may occur in various vicinities throughout the country which oxidation may be instituted in a gasoline, gas oil, other petroleum fractions or in the crude itself. This oxidation could be brought about for example by treatment with nitric acid in which case the oxidation products, being soluble in the nitric acid, will be separated from the oil in the aqueous phase and may be recovered therefrom to be in turn added to the Diesel fuel to be treated. Perhaps the most feasible chemical method of utilization involves the preparation of the sulfoxides from comparatively pure compounds by the controlled oxidation or combined sulfonation and oxidation of such compounds as described above, and subsequent addition to the sulfoxides or sulfones to Diesel fuel. As an alternative to these methods I may add sulfoxides and sulfones directly to the combustion chamber of a compression ignition engine simultaneously with the fuel by introduction into the fuel at the point of injection or by injection into the combustion chamber simultaneously with but isolated from the fuel injection. This type of operation would enhance the initial relatively low temperature combustion of the ignition accelerator due to its comparative isolation from the fuel.

In normal operation, however, it is preferable to add these oxidized sulfur compounds to the Diesel fuels at other sources prior to the shipment and storage. I have found that these compounds are stable under ordinary storage conditions and may therefore be added to the fuel at any convenient time prior to its use. The amount of these oxygenated sulfur compounds which may be added to a Diesel fuel would be dependent upon the characteristics of the Diesel fuel employed and in the desired increase of the cetane value of the fuel. We have found that quantities of from 0.1% to 3% and even as high as 5% by volume of these compounds may be satisfactorily employed with best results being realized upon the addition of from about 0.5% to about 2% of the sulfoxides or sulfones.

The foregoing description and examples of my invention are not meant to be limiting inasmuch as many modifications will occur to those skilled in the art without departing from the spirit and scope of the following claims:

I claim:

1. A composition of matter consisting essentially of a petroleum hydrocarbon fraction boiling within the limits of about 300° F. to about 800° F. and 0.1% to 5% by volume of an oxidized organic sulfur compound selected from the class of compounds consisting of organic sulfoxides and organic sulfones the organic radicals being selected from the group consisting of lower alkyls, phenyl, benzyl, and organic sulfur compounds in which the organic group is heterocyclic, the heterocyclic ring having up to six atoms and containing from 1 to 3 sulfinyl groups in the ring.

2. A composition of matter consisting essentially of a petroleum hydrocarbon fraction boiling within the limits of about 300° F. to about 800° F. and between about 0.1% and 5% by volume of an organic sulfur compound the organic group being a heterocyclic radical having up to six atoms in the ring and containing from 1 to 3 sulfinyl groups in the ring.

3. A Diesel fuel of improved ignition characteristics consisting essentially of a petroleum hydrocarbon fraction boiling within the limits of about 300° F. to about 800° F. to which has been added between about 0.1% and 5% by volume of an oxidized organic sulfur compound selected from the class of compounds consisting of organic sulfoxides and organic sulfones, the organic radicals being selected from the group consisting of lower alkyls, phenyl, benzyl, and organic sulfur compounds in which the organic group is heterocyclic, the heterocyclic ring having up to six atoms and containing from 1 to 3 sulfinyl groups in the ring.

4. A petroleum hydrocarbon fraction boiling between the limits of about 300° F. to about 800° F. useful as a Diesel fuel and 0.1% to 5% by volume of sulfoxides produced in situ therein from sulfur compounds in such hydrocarbon fraction.

5. A petroleum hydrocarbon fraction boiling between the limits of about 300° F. to about 800° F. useful as Diesel fuel and 0.1% to 5% by volume of sulfoxides produced in situ therein from alkyl sulfides and alkylated thiophanes in such hydrocarbon fraction.

6. A composition of matter according to claim 1 in which said oxidized organic sulfur compound is an organic sulfoxide.

7. A composition of matter according to claim 1 in which said oxidized organic sulfur compound is an organic sulfone.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,257,969	Loane et al.	Oct. 7, 1941
2,326,102	Nygaard et al.	Aug. 3, 1943
2,355,261	Seger et al.	Aug. 8, 1944

Certificate of Correction

Patent No. 2,493,284

January 3, 1950

ADALBERT FARKAS

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 7, line 26, for "OR, SR, X, NR''R where R and R'" read *OR'', SR'', X, NR''R'' where R''*;

and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 16th day of May, A. D. 1950.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.