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STABILIZED PETROLEUM OIL DISTILLATES

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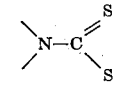
13 Claims. (Cl. 44—9)

This invention relates to stabilized petroleum oil distillates.

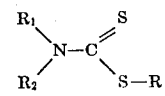
In the refining of petroleum oils a number of the distillates obtained are inherently subject to autoxidation and resulting deterioration which fact greatly impairs the usefulness of the products affected thereby and renders the same in many instances unit for the purposes for which they are intended. This autoxidative deterioration is particularly attendant upon the lighter cracked hydrocarbon fractions such as kerosene, gasoline, etc. and upon some of the highly refined heavier fractions such as medicinal white oils. Thus, for instance, a cracked gasoline will gradually precipitate gummy substances which are very detrimental to its use as a motor fuel while medicinal white oils will develop a highly undesirable and objectionable rancid odor and taste. In all these cases of autoxidation of petroleum distillates the cause is substantially the same and only the manifestation of the reaction differs in each particular case.

The first stage of autoxidative deterioration of petroleum oil distillates is the formation of peroxides and the time which elapses until the first peroxide formation can be observed is regarded as a criterion of the stability of a given product. Under ordinary conditions such time element is expressed in weeks or months but by subjecting an oil distillate to high temperatures the time elapsing until the first traces of peroxide formation appear may be expressed in minutes and is then commonly termed in petroleum refining technology the induction period of the oil distillate and serves as a practical measure for the relative stability of the product. One common practice for the determination of the induction period is to heat the distillate to be tested in quantities of 10 cc. in stoppered test tubes in an oil bath kept at 300° F. for convenient intervals, as a rule multiples of 5 minutes. The peroxide test as such may be carried out by shaking the oil to be tested with an aqueous acetone solution of ferrous thio-cyanate which will show a red coloration at the first sign of peroxide formation as the result of the conversion of the ferrous to ferric thiocyanate. Where in the specification and claims, therefore, I use the term induction period in connection with an oil distillate inherently subject to autoxidation I mean to define thereby the period which elapses until the first traces of peroxide formation appear in the distillate while the same is heated at a temperature of approximately 300° F.

I have discovered that I can substantially stabilize petroleum oil distillates and substantially inhibit any inherent autoxidation and resulting deterioration of such products by the addition of comparatively small amounts of substances having in their molecular structure at least once the grouping



in open chain configuration and of the general formula



in which R_1 or R_2 or both may represent hydrogen or any aliphatic or aromatic or mixed aliphatic aromatic or heterocyclic radical and in which R may represent any aliphatic or aromatic or mixed aliphatic aromatic or heterocyclic radical or any metal radical including the ammonium radical and aliphatic or aromatic or mixed aliphatic aromatic substituted ammonium radical. Substances of the afore-described nature may be generally classified as dithiocarbamic acid compounds such as dithiocarbamic acid salts or ethers, ammonium dithiocarbamate, mono or di-alkyl-ammonium monor or di-alkyl-dithiocarbamate as well as the aryl, aralkyl, aryl-aralkyl, aryl-alkyl including heterocyclic derivatives of these products. Thus where I use in the specification and claims the term "dithiocarbamic acid compound" or such similar expression I mean to embrace substances of the afore-described character and nature as well as mixtures thereof.

In the practical application of my invention the dithiocarbamic acid compound is added to the distillate to be treated in small amounts sufficient to raise the normal induction period of the same and to substantially effectuate thereby a stabilization to the desired extent. Though substantially absolute and permanent stabilization may be obtained it will in many cases suffice for practical purposes to achieve a stabilization equivalent to an induction period in excess of twice the induction period of the untreated distillate. This result may be obtained by additions of 0.001% and in some cases as low as 0.0001% of the dithiocarbamic acid compound.

In manufacturing a commercial product, however, I prefer to obtain an induction period of at least 50 minutes which is equivalent to a stabilization under atmospheric conditions and even constant exposure to sunlight for a period in excess of 6 months which in most cases is regarded as sufficiently stable and I have found additions of 0.01% to 0.001% of sufficient potency for such purposes.

Concerning the method of addition of the dithiocarbamic acid compound I have found that

when the amount used is within the range of substantial solubility in the distillate, (e. g. lower concentrations), the particular mode of addition is not very critical and the substance may be added either in solid form or in the form of a solution in a suitable solvent. When, however, the amount of dithiocarbamic acid compound used is substantially beyond such range and practically within the range of substantial insolubility, (e. g. higher concentrations), I have discovered as a further embodiment of my invention that the potency of the dithiocarbamic acid compound may be greatly enhanced by adding the same to the distillate not in solid form to be suspended therein but in the form of a solution in a solvent which as between the oil distillate and the dithiocarbamic acid compound will preferentially dissolve the latter being at the same time completely miscible with the former. In this manner it is possible in most instances to obtain induction periods of twice those obtainable with dithiocarbamic acid compound suspensions. The selection of the particular solvent used in this connection depends upon the particular dithiocarbamic acid compound used in its preferential solvent power relation to the particular distillate sought to be treated. I have found, however, that in the majority of cases satisfactory results are obtained with a solution of the inhibitor compound in ether, alcohol or acetone. No critical limitations exist with regard to the concentration of inhibitor compounds in the preferential solvent; it is of course understood that the concentration shall be sufficiently low to prevent separation of solid inhibitor particles at low temperatures. The addition of the inhibitor in its preferential solvent solution is preferably effected in the cold.

The following tabulations are illustrative of practical embodiments of the invention but are in no way to be taken as indicative of the scope thereof:

TABLE I

Dimethyl-ammonium dimethyl-dithiocarbamate $(CH_3)_2N.CSSNH_2(CH_3)_2$

Concetration of inhibitor	Induction period			
	White oil inhibitor suspension	White oil inhibitor in ethereal solution	Kerosene inhibitor in ethereal solution	Gasoline inhibitor in ethereal solution
	Minutes	*Minutes*	*Minutes*	*Minutes*
0.1	Over 180	Over 180	Over 180	Over 160
0.01	Over 110–120	Over 180	Over 95–100	Over 120
0.001	Over 30–35	Over 75–80	Over 60–65	Over 85
0.0001	Over 20–25	Over 35–40	Over 25–28	Over 30–35
Normal induction period	10	10	3–4	10–12

TABLE II

Sodium diethyl-dithiocarbamate $(C_2H_5)_2N.CSSNa$

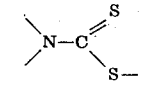
Concentration of inhibitor	Induction period			
	White oil inhibitor suspension	White oil inhibitor in ethereal solution	Kerosene inhibitor in ethereal solution	Gasoline inhibitor in ethereal solution
	Minutes	*Minutes*	*Minutes*	*Minutes*
0.1	85–90	Over 180	Over 180	Over 180
0.01	45–50	Over 65–70	Over 65–70	Over 65–70
0.001	20–25	Over 20–25	Over 20–25	Over 20–25
Normal induction period	10	10	3–4	10–12

As representative inhibitors sodium diethyl-dithiocarbamate and dimethyl-ammonium dimethyl-dithiocarbamate respectively were used and are shown in various concentrations in relation to their effectiveness as stabilizers on a number of petroleum oil distillates inherently subject to autoxidation as expressed in terms of induction periods. The last three columns in each table list the induction periods of inhibitor added in preferential solution whereas the second column demonstrates induction periods of inhibitor suspensions. Amounts of 0.0001% dimethyl-ammonium dimethyl-dithiocarbamate or 0.001% sodium diethyl-dithiocarbamate respectively are practically within the range of substantial solubility in either of the distillates used and the respective induction periods do not materially differ whether the particular inhibitor is added in solid form or in the form of a preferential solvent solution as for instance in ether. Amounts, however, in excess of 0.0001% dimethyl-ammonium dimethyl-dithiocarbamate or 0.001% sodium diethyl-dithiocarbamate are practically within the range of substantial insolubility in either of the distillates and additions of the respective inhibitors in preferential solvent solution result in markedly higher induction periods than corresponding additions of such inhibitors in solid form.

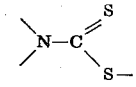
The foregoing description is by way of illustration and not of limitation and I am not to be limited to any details but only by the appended claims in which I have endeavored to claim broadly all inherent novelty.

I claim:

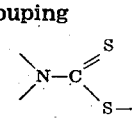
1. A petroleum oil distillate composition comprising a petroleum oil distillate inherently subject to autoxidation having normally a low induction period and a small amount of a dithiocarbamic acid compound sufficient to raise the normal induction period of said distillate said compound possessing in open chain configuration at least once the grouping



2. A petroleum oil distillate composition comprising a petroleum oil distillate inherently subject to autoxidation having normally a low induction period and a small amount of a dithiocarbamic acid compound sufficient to raise the normal induction period of said distillate to at least twice the normal period said compound possessing in open chain configuration at least once the grouping

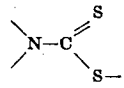


3. A petroleum oil distillate composition comprising a petroleum oil distillate inherently subject to autoxidation having normally an induction period of less than 50 minutes and a small amount of a dithiocarbamic acid compound sufficient to raise the normal induction period of said distillate to at least 50 minutes said compound possessing in open chain configuration at least once the grouping

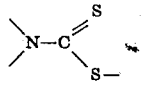


4. A petroleum oil distillate composition comprising a cracked kerosene having normally a

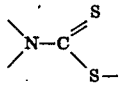
v induction period and a small amount of a hiocarbamic acid compound sufficient to raise e normal induction period of said kerosene said mpound possessing in open chain configuration least once the grouping



5. A petroleum oil distillate composition comising a cracked gasoline having normally a low luction period and a small amount of a dithiorbamic acid compound sufficient to raise the rmal induction period of said gasoline, said mpound possessing in open chain configuration least once the grouping



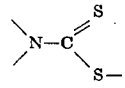
6. A petroleum oil distillate composition comising a medicinal white oil having normally a v induction period and a small amount of a dilocarbamic acid compound sufficient to raise e normal induction period of said medicinal ute oil said compound possessing an open chain nfiguration at least once the grouping



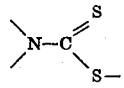
7. A petroleum oil distillate composition comising a medicinal white oil having normally a v induction period and a small amount of an yl dithiocarbamate sufficient to raise the norl induction period of said medicinal white oil.

8. A petroleum oil distillate composition comising a medicinal white oil having normally a v induction period and a small amount of an yl-ammonium alkyl-dithiocarbamate sufficient raise the normal induction period of said dicinal white oil.

9. A petroleum oil distillate composition comprising a petroleum oil distillate inherently subject to autoxidation having normally a low induction period and a small amount of a solution of a dithiocarbamic acid compound in a solvent in which said derivative as compared with said distillate is preferentially soluble, said solvent being completely miscible with said distillate, said solution being present in amount sufficient to raise the normal induction period of said distillate, said compound possessing in open chain configuration at least once the grouping



10. A petroleum oil distillate composition comprising a white oil having normally a low induction period and a small amount of a solution of a aliphatic dithiocarbamate in ether, sufficient to raise the normal induction period of said white oil, said compound possessing in open chain configuration at least once the grouping



11. A petroleum oil distillate composition in accordance with claim 1 in which said di-thiocarbamic acid compound is an alkyl di-thiocarbamate.

12. A petroleum oil distillate composition in accordance with claim 1 in which said di-thiocarbamic acid compound is an alkyl ammonium alkyl di-thiocarbamate.

13. A petroleum oil distillate composition comprising a medicinal white oil inherently subject to autoxidation and a small amount of an aliphatic dithiocarbamate sufficient to substantially inhibit autoxidation of said medicinal white oil.

JACOB FAUST.

CERTIFICATE OF CORRECTION.

Patent No. 2,160,851. June 6, 1939.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, first column, line 8, for the word "unit" read unfit; same page, second column, line 26, for "monor" read mono; page 3, second column, line 6, claim 9, for the word "derivative" read compound; 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 1st day of August, A. D. 1939.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.