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STABILIZATION OF VISCOUS PETROLEUM OILS

Frederick B. Downing and Charles J. Pedersen, Penns Grove, N. J., assignors to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

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This invention relates to the color stabilization of viscous petroleum oils, and particularly to the protection of viscous petroleum oils against the deleterious action of oxygen and metals on the color of such oils during storage.

One of the problems confronting the petroleum refiner is the preservation of the finished products from the time of manufacture to their ultimate consumption. These products are frequently subjected to long storage or to adverse atmospheric conditions which cause their deterioration. In the case of lubricating oils, the loss of quality is manifested by color darkening. Since color and color stability are still indices of refining skill, the development of color during storage may eventually lead to failure to meet specifications.

Although the color of most lubricating oils will increase in time the process is a relatively slow one at normal atmospheric temperatures. In order to expedite the testing of oils, therefore, accelerated methods are used.

There are three main factors contributing to the darkening of color, namely, oxygen, temperature and catalysts. Of these three, temperature is the most effective and readily controlled in accelerating color formation and is usually used for this purpose.

Some success has been obtained in recent years in preventing the color deterioration of viscous petroleum oils by adding thereto compounds generally called "oxidation inhibitors," "antioxidants" and "color stabilizers." Most of such agents are oxidizable organic substances which are oxidized in the course of time whereby their beneficial effect is not permanent. They protect the oil only so long as they are not rendered inactive. They are, moreover, very specific in their action, each type of autoxidizable substance requiring a different type of compound for the best results.

It is well known that copper and its compounds accelerate the rate of oxidation of oxidizable organic substances, including most of the antioxidants. Accordingly, copper and antioxidents are antagonistic in action and the normal effect of the antioxidant is greatly reduced in the presence of copper and its compounds. Frequently, the viscous petroleum oils come into contact with vessels and conduits made of metals containing copper whereby the oil becomes contaminated with the copper or its compounds. Also, copper, or its compounds, is sometimes used in refining processes. Accordingly, the viscous petroleum oils are frequently contaminated with small amounts of copper and its compounds. Furthermore, the viscous petroleum oils, in use, come into contact with metals, such as iron and aluminum and bearing metals such as silver-cadmium alloys, copper-lead alloys and babbitt, which accelerate the formation of color in the oil, apparently due to a catalytic action.

An object of the present invention is to provide means for stabilizing the color of viscous petroleum oils. Another object is to protect viscous petroleum oils against the deleterious action of oxygen and metals. A further object is to provide a class of compounds which, when added to viscous petroleum oils, retards the action of oxygen, heat and metals in causing color formation without harmfully affecting the other properties of the oils. Still further objects are to provide new compositions of matter and to advance the art. Still other objects will appear hereinafter.

The above and other objects may be accomplished in accordance with our invention which comprises incorporating, in viscous petroleum oils which are subject to deterioration in color, organic compounds of the type of Schiff's bases, obtained by condensing one mol of an aliphatic polyamine, containing at least two primary amino groups capable of reacting with aromatic aldehydes to form arylidene amines, with at least two mols of an aldehyde, so that not more than one mol of aldehyde reacts for each primary amino group of the amine.

The polyamine may be any aliphatic amine containing at least two primary amino groups directly attached to different carbon atoms of the same open chain and which amine may contain aromatic or other cyclic groups substituted on the chain. The open chain may contain elements other than carbon, such as nitrogen, oxygen and sulfur as in di-(2-hydroxy benzal) triethylene tetramine, di-(2-hydroxy benzal) di-(b-aminoethyl) sulfide and di-(2-hydroxy benzal) di-(b-aminoethyl) ether. The term "aliphatic polyamine," as employed hereinafter and in the claims, will be understood to have the foregoing meaning. The preferred polyamines are those consisting of carbon, hydrogen and nitrogen, those in which at least two primary amino groups are directly attached to adjacent carbon atoms, and particularly the diamines.

The aldehyde may be aliphatic or aromatic, but is preferably aromatic. When the oil to be treated is free of metal compounds tending to catalyze deterioration of the oil and the oil is employed out of contact with such catalytic metals or catalytically active compounds thereof, the

aldehyde is preferably unsubstituted. However, when the oil contains or is in contact with catalytically active metals or their catalytically active compounds, the aldehyde is preferably an ortho-hydroxy substituted aromatic aldehyde. In this later case, the aldehyde is also preferably one devoid of substituents other than hydrocarbon, alkoxy and hydroxy groups. Also, preferably, the aldehyde contains only a single hydroxy group. However, such aldehyde may contain, as substituents, aryloxy, halogen, heterocyclic, amino, nitro, cyano and carboxyl groups, as well as hydroxy, alkoxy, alkyl and aryl radicals. The polyamine may be likewise substituted but is preferably unsubstituted.

By "adjacent atoms," we mean atoms directly bonded together. By an "ortho-hydroxy substituted aromatic aldehyde," we mean one in which the hydroxy group and the aldehyde, or —CHO, group are directly bonded to adjacent ring carbon atoms. By the term "aldehyde, aromatic in nature," we intend to include the unsaturated cyclic aldehydes, such as the pyridine and quinoline aldehydes, which have many of the characteristic properties of the aromatic aldehydes, as well as the strictly aromatic aldehydes in which the hydroxy and aldehyde groups are bonded to nuclear carbon atoms of an aromatic ring.

The compounds of the type of Schiff's bases, employed in accordance with our invention, may be represented by the formulae

(1) A—CH=N—R—N=CH—B and, preferably,

(2) HO—A—CH=N—R—N=CH—B—OH

wherein A and B each represents an organic radical and preferably a hydrocarbon radical. In Formula 2 A and B each preferably represents an aromatic ring or an unsaturated heterocyclic ring in which the hydroxyl radical is attached directly to a ring carbon atom ortho to the —CH=N group. R represents an aliphatic radical having the two N atoms attached directly to different carbon atoms of the same open chain.

Definite operative concentrations cannot be specified as to all oils, as the quantity required will vary for different oil samples. Some oils will require only 0.01% or less, while others will require 0.1% or more. The upper limit is fixed by the solubility of the compounds in the oils. For example, the solubility of di-(2-hydroxy benzal) ethylene diamine, in the viscous petroleum oils, is about 0.4 to 0.5% by weight at 70° F. and about 1.75 to about 2.5% by weight at 200° F. Ordinarily, from about 0.002 to about 1% by weight will be satisfactory for most oils. Preferably, from about 0.01 to about 0.1% will be used. When the oils contain compounds of copper or other metals tending to accelerate deterioration of the oil, the amount of compound employed will generally be from about 1.5 to 100 mols for each atom of metal in the oil. When the oil is in contact with catalytic metal in bulk form, it will frequently be desirable to use a substantially saturated solution of the compound in the oil.

The data presented in the following tables were obtained by heating 50 grams of the oil in a 250 cc. Pyrex beaker open to the air at 300° F. for six hours and then comparing the color of the oil before and after this treatment. The color measurements are given in units of a scale of true color in which 1 is equal to N. P. A. Color Number 1. In some of the tests, the effects of different metals were obtained by immersing the strips of the metals in the oil under test.

Table I shows the action of several members of the new class of color stabilizers on a sample of lubricating oil.

TABLE I

Oil sample: distilled Gulf Coast S. A. E. 30.
Temperature and duration of tests: 300° F. for 6 hours.
Initial true color of the oil: 11.

No.	Stabilizer	Conc. weight	True color after test	Increase in color	Inhibition of color formation
		Percent		*Percent*	*Percent*
1	None (control)	-------	67	509	0
2	Di-(2-hydroxy-3-methoxybenzal) ethylenediamine	0.1	18	64	87
3	Di-(2-hydroxybenzal) ethylenediamine	0.1	20	82	84
4	Di-(2-hydroxybenzal) decamethylenediamine	0.1	20	82	84
5	Di-(2-hydroxybenzal) triethylenetetramine	0.1	20	82	84
6	Di-(2-hydroxybenzal) hexamethylenediamine	0.1	22	100	80
7	Di-(2-hydroxybenzal) 1:3-propylenediamine	0.1	24	118	77
8	Di-(2-hydroxybenzal) di-(b-aminoethyl) sulfide	0.1	28	155	70

It is readily seen that all these compounds stabilize the color of the lubricating oil, although there is some variation in their effectiveness.

Di-(2-hydroxybenzal) ethylenediamine, stabilizer No. 3 of Table I, was selected for more detailed illustration. The effect of varying the concentration of this compound is shown in Table II.

TABLE II

Oil sample: solvent extracted Mid-Continent S. A. E. 20.
Temperature and duration of tests: 300° F. for 12 hours.
Initial true color of the oil: 24.

No.	Stabilizer	Conc. weight	True color after test	Increase in color	Inhibition of color formation
		Percent		*Percent*	*Percent*
1	None (control)	-------	283	1,081	0
2	Di-(2-hydroxybenzal) ethylenediamine	0.01	67	179	83
3	do	0.02	62	158	85
4	do	0.03	56	133	88
5	do	0.04	49	104	90
6	do	0.05	49	104	90

It is evident that only 0.01% of the compound is required to stabilize this oil. It was found, however, that some other oils required from 0.02 to 0.03% for sufficient stabilization.

The action of di-(2-hydroxybenzal) ethylene diamine on a lubricating oil at different temperatures is represented in Table III.

TABLE III

Oil sample: solvent extracted Mid-Continent S. A. E. 20.
A: oil not stabilized (control).
B: oil stabilized with 0.05 to 0.1% di-(2-hydroxy-benzal) ethylenediamine.
Initial true color of the oil: 26.

Temperature	Duration of tests	True color after test		Increase in color		Inhibition of color formation	
		A	B	A	B	A	B
° F.	*Hours*			*Percent*	*Percent*	*Percent*	*Percent*
153	867	62	35	138	35	0	75
207	671	135	49	419	88	0	79
300	6	125	38	381	46	0	88
329	6	220	56	746	115	0	85

It is seen that di-(2-hydroxybenzal) ethylenediamine functions satisfactorily up to at least 329° F.

The effects of different metals on the darkening of the color of lubricating oil and how di-(2-hydroxybenzal) ethylenediamine retards this process in the presence of these metals are shown in Table IV.

TABLE IV

Oil sample: distilled Gulf Coast S. A. E. 30.
Temperature and duration of tests: 300° F. for 6 hours.
Initial true color of the oil: 10.

No.	Metal	Dimensions of metal strips	Conc. of inhibit.	True color after test	Increase in color	Inhibition color formation
		Mm.	*Weight percent*		*Percent*	*Percent*
1	None		0.0	82	720	0
2	do		0.1	24	140	81
3	Silver-cadmium alloy	35 x 10 x 2	0.0	135	1,250	0
4	do	35 x 10 x 2	0.1	28	180	86
5	Cast aluminum (8.1% Cu).	37 x 11 x 3	0.0	380	3,700	0
6	do	37 x 11 x 3	0.1	31	210	94
7	Iron	51 x 10 x 0.5	0.0	690	6,800	0
8	do	51 x 10 x 0.5	0.1	35	250	96
9	Babbitt	45 x 10 x 2	0.0	930	9,200	0
10	do	45 x 10 x 2	0.1	31	210	98
11	Copper-lead alloy	37 x 10 x 2	0.0	1,090	10,800	0
12	do	37 x 10 x 2	0.1	35	250	96

Thus compounds belonging to this new class of color stabilizers are not only capable of retarding the darkening of the color of lubricating oils, but also of counteracting the catalytic effects of metals.

In the following tables, the color measurements are given in N. P. A. No.'s as determined by means of an A. S. T. M. Union Colorimeter.

The data presented in Table V show the inhibition of color formation in a sample of oil by several other members of the new class of color stabilizers.

TABLE V

Inhibition of color formation at 300° F.

Oil sample: distilled Gulf Coastal S. A. E. 30
Duration of tests: 6 hours.
Concentration of stabilizer in the oil: 0.1% by weight.
Initial color of the oil: N. P. A. No. 2½.

No.	Stabilizer	Color of oil after the test	Color increment
		N. P. A. number	*N. P. A. units*
1	None (control)	5	2½
2	Dibenzal ethylenediamine	3	½
3	Dibenzal hexamethylenediamine	3½	1
4	Dibenzal diethylenetriamine	3	½
5	Dibenzal triethylenetetramine	3	½
6	Dipropional ethylenediamine	3½	1
7	Di-(n-butyral) ethylenediamine	3	½
8	Di-(n-butyral) hexamethylenediamine	3	½
9	Di-(p-totual) propylenediamine	3	½
10	Di-(p-anisal) propylenediamine	3	½
11	Disalicylal ethylenediamine	3	½

It is readily seen that at 0.1% by weight all these compounds decrease the amount of color developed in the oil. They also function in oils produced from other crudes, such as Mid-Continent and Pennsylvania.

In order to determine the effect of concentration a number of tests were run with portions of oil containing different quantities of dibenzal ethylenediamine, one of the color stabilizers shown above. The results of these tests are given in Table VI.

TABLE VI

The effect of concentration of dibenzal ethylenediamine

Oil sample: distilled Gulf Coastal S. A. E. 30.
Duration and temperature of tests: 6 hours at 300° F.
Initial color of the oil: N. P. A. No. 2½.

Number	Concentration of dibenzal ethylenediamine	Color of oil after the test	Color increment
	Percent by weight	*N. P. A. number*	*N. P. A. units*
1	0	4½	2
2	0.1	3	½
3	0.05	3	½
4	0.01	3	½
5	0.005	4½	2

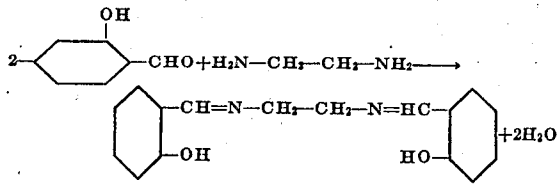
It is evident that only 0.01% of this compound is required to retard color formation in this sample of oil. It was found, however, that some other oils took from 0.02 to 0.03% for sufficient stabilization.

The compounds of Tables V and VI are very effective in the absence of metals and their compounds which tend to catalyze the deterioration of the oils but are less effective than the ortho-hydroxy substituted compounds in the presence of such metals and their compounds. They do not cause the oils to lose brilliancy and do not form insoluble residues with the acids formed in the oils.

About twenty-five other samples of lubricating oils were tested and found to respond favorably to treatment with our compounds and none of the oils were affected harmfully by such compounds.

The color stabilizers of our invention are easily prepared in accordance with known methods such as by reacting the required molal proportions of polyamines and aldehydes with or without the use of a suitable solvent, such as water, methanol or ethanol. The reactions are exo-

thermic and water is formed. Nearly theoretical yields of the compounds are obtained. The chemical equation for the formation of di-(2-hydroxybenzal) ethylenediamine is:



They are only slightly soluble in water and are not readily extracted by it from oils. Unlike the common antioxidants, they are resistant to the action of molecular oxygen and may be kept in contact with air for years without any apparent change. They are thermally stable to above their melting points, but are destroyed by strong mineral acids or hot dilute mineral acids. They are generally colored yellow of varying shades and intensity.

These color stabilizers may be added to the oils in any form and manner. They may be in solid or liquid form, mixed with other addition agents or dissolved in a solvent. They are compatible with other adjuvants and have no detrimental effects on properties of oils, such as pour-point, viscosity index, sludging in accelerated tests, flash, fire, Conradson carbon, corrosiveness and film strength.

Although our compounds find their principal use in preventing color deterioration of finished lubricating oils in storage, they may also be used in refinery processes for reducing color darkening where it is necessary to heat the oils such as in filtration and naphtha stripping after dewaxing. Accordingly, our compounds may be added either to the finished oils or to the oils at any stage in the process of their manufacture subsequent to acid treatment.

We have also found our compounds to be effective in retarding color formation in fuel oils and oils used in heat transfer apparatus and electrical transformers and in greases. Accordingly, by viscous petroleum oils, we intend to include such oils as well as lubricating oils, but intend to exclude the light non-viscous oils such as gasoline and kerosene.

Besides the compounds hereinbefore specifically mentioned and many others, the compounds, obtained by condensing each of the following aldehydes with each of the following polyamines, will be effective color stabilizers in accordance with our invention.

Aldehydes

Benzaldehyde
2-methylbenzaldehyde
3-methylbenzaldehyde
4-methylbenzaldehyde
2-methoxybenzaldehyde
4-methoxybenzaldehyde
a-naphthaldehyde
b-naphthaldehyde
4-phenylbenzaldehyde
Propionaldehyde
n-Butyraldehyde
Heptaldehyde
Aldol
2-hydroxybenzaldehyde
2-hydroxy-6-methylbenzaldehyde
2-hydroxy-3-methoxybenzaldehyde
2-4-dihydroxybenzaldehyde
2-6-dihydroxybenzaldehyde
2-hydroxynaphthaldehyde-1
1-hydroxynaphthaldehyde-2
Anthrol-2-aldehyde-1
2-hydroxyfluorene-aldehyde-1
4-hydroxydiphenyl-aldehyde-3
3-hydroxyphenanthrene-aldehyde-4
1-3-dihydroxy-2-4-dialdehydebenzene
2-hydroxy-5-chlorobenzaldehyde
2-hydroxy-3:5-dibromobenzaldehyde
2-hydroxy-3-nitrobenzaldehyde
2-hydroxy-3-cyanobenzaldehyde
2-hydroxy-3-carboxybenzaldehyde
4-hydroxypyridine-aldehyde-3
4-hydroxyquinoline-aldehyde-3
7-hydroxyquinoline-aldehyde-8

Polyamines

Ethylenediamine
1-2-propylenediamine
1-3-propylenediamine
1-6-hexamethylenediamine
1-10-decamethylenediamine
Diethylenetriamine
Triethylenetetramine
Pentaerythrityltetramine
1-2-diaminocyclohexane
Di-(b-aminoethyl) ether
Di-(b-aminoethyl) sulfide

The compounds employed need not be pure compounds, but may be mixtures of two or more of the compounds hereinbefore indicated, as well as products obtained by the condensation of a given polyamine with a mixture of aldehydes, or the condensation of a given aldehyde with a mixture of polyamines, so long as the aldehydes, polyamines and reaction products fall within the classes hereinbefore defined.

While we have disclosed the preferred embodiments of our invention and the preferred modes of carrying the same into effect, it will be readily apparent to those skilled in the art that many variations and modifications may be made therein without departing from the spirit of our invention. Accordingly, the scope of our invention is not to be limited solely by the specific examples disclosed herein.

We claim:

1. A viscous petroleum oil normally subject to deterioration in color having incorporated therein a small amount of an organic compound of the type of a Schiff's base, obtained by condensing 1 mol of an aliphatic polyamine containing at least two primary amino groups directly attached to different carbon atoms of the same open chain with at least 2 mols of an aldehyde, so that one and only one mol of aldehyde reacts for each primary amino group of the polyamine.

2. A viscous petroleum oil normally subject to deterioration in color having incorporated therein a small amount of an organic compound of the type of Schiff's base, obtained by condensing 1 mol of an aliphatic polyamine containing only two primary amino groups directly attached to different carbon atoms of the same open chain with 2 mols of an aromatic aldehyde, so that one and only one mol of aldehyde reacts for each primary amino group of the polyamine.

3. A viscous petroleum oil normally subject to deterioration in color having incorporated therein a small amount of an organic compound of the type of Schiff's base, obtained by condensing 1 mol of an alkyl diamine in which the amino groups are primary amino groups directly attached to adjacent carbon atoms of the same open chain with 2 mols of an aromatic aldehyde consisting of the elements carbon, hydrogen and oxygen, so that one and only one mol of aldehyde reacts for each primary amino group of the amine.

4. A viscous petroleum oil normally subject to deterioration in color having incorporated therein a small amount of dibenzal ethylene diamine.

5. A viscous petroleum oil normally subject to deterioration in color having incorporated therein a small amount of disalicylal ethylene diamine.

6. A viscous petroleum oil normally subject to deterioration in color in the presence of a catalytically active metal, having incorporated therein a small amount of an organic compound of the type of Schiff's base, obtained by condensing 1 mol of an aliphatic polyamine containing at least two primary amino groups directly attached to different carbon atoms of the same open chain with at least 2 mols of an ortho-hydroxy substituted aromatic aldehyde, so that one and only one mol of aldehyde reacts for each primary amino group of the polyamine.

7. A viscous petroleum oil normally subject to deterioration in color in the presence of a catalytically active metal, having incorporated therein a small amount of an organic compound of

the type of Schiff's base, obtained by condensing 1 mol of an aliphatic polyamine containing only two primary amino groups attached to different carbon atoms of the same open chain with 2 mols of an ortho-hydroxy substituted aromatic aldehyde consisting of the elements carbon, hydrogen and oxygen, so that one and only one mol of aldehyde reacts for each primary amino group of the polyamine.

8. A viscous petroleum oil normally subject to deterioration in color in the presence of a catalytically active metal, having incorporated therein a small amount of disalicylal ethylene diamine.

9. A viscous petroleum oil normally subject to deterioration in color having incorporated therein a small amount of an organic compound of the type of Schiff's base, obtained by condensing 1 mol of an aliphatic polyamine containing at least two primary amino groups directly attached to different carbon atoms of the same open chain with at least 2 mols of an aromatic aldehyde, so that one and only one mol of aldehyde reacts for each primary amino group of the polyamine.

10. A viscous petroleum oil normally subject to deterioration in color having incorporated therein a small amount of an organic compound of the type of Schiff's base, obtained by condensing 1 mol of an aliphatic diamine in which the amino groups are primary amino groups directly attached to different carbon atoms of the same open chain with 2 mols of an aromatic aldehyde consisting of the elements carbon, hydrogen and oxygen, so that one and only one mol of aldehyde reacts for each primary amino group of the polyamine.

11. A viscous petroleum oil normally subject to deterioration in color having incorporated therein a small amount of an organic compound of the type of Schiff's base, obtained by condensing 1 mol of an alkyl diamine in which the amino groups are primary amino groups directly attached to different carbon atoms of the same open chain with 2 mols of an aromatic aldehyde free of substituents other than hydrocarbon radicals, so that one and only one mol of aldehyde reacts for each primary amino group of the amine.

12. A viscous petroleum oil normally subject to deterioration in color in the presence of a catalytically active metal, having incorporated therein a small amount of an organic compound of the type of Schiff's base, obtained by condensing 1 mol of an aliphatic polyamine containing at least two primary amino groups directly attached to different carbon atoms of the same open chain with at least 2 mols of a hydroxy substituted aldehyde, aromatic in nature, in which the hydroxy group and the —CHO group are directly bonded to adjacent ring carbon atoms, so that one and only one mol of aldehyde reacts for each primary amino group of the polyamine.

13. A viscous petroleum oil normally subject to deterioration in color in the presence of a catalytically active metal, having incorporated therein a small amount of an organic compound of the type of Schiff's base, obtained by condensing 1 mol of an aliphatic polyamine containing at least two primary amino groups attached to different carbon atoms of the same open chain with at least 2 mols of an ortho-hydroxy substituted aromatic aldehyde consisting of the elements carbon, hydrogen and oxygen, so that one and only one mol of aldehyde reacts for each primary amino group of the amine.

14. A viscous petroleum oil normally subject to deterioration in color having incorporated therein a small amount of di-(n-butyral) ethylene diamine.

FREDERICK B. DOWNING.
CHARLES J. PEDERSEN.