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UNITED STATES PATENT OFFICE

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COMPOSITION OF MATTER

George Entwistle and Henry John Voss, Chicago, Ill., assignors to Sinclair Refining Company, New York, N. Y., a corporation of Maine

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5 Claims. (Cl. 252—42.4)

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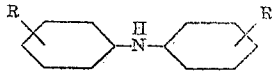
Our invention relates to the manufacture of lubricating greases and more particularly relates to stabilization of grease compositions against deterioration through oxygen instability. It provides new grease compositions characterized by improved resistance to deterioration through oxidation.

Lubricating greases in general are susceptible to oxidation in storage and in service despite care in formulation and fabrication and reasonable precautions taken in the selection of raw materials. When a grease oxidizes in service, its structure deteriorates and oxidized oil and rancid soap particles are produced. The affected grease fails to give the proper lubrication to the bearings or other moving parts for which it was intended and thus exposes them to mechanical failure. In service, deterioration by oxidation is accelerated by elevated operating temperatures and the aeration caused by revolving mechanical parts. We have studied the availability and serviceability of a large number of materials which have been proposed as antioxidants for incorporation into grease compositions. We have found it difficult however to find substances which are compatible with the grease components, which do not affect the color, appearance or odor of the finished grease, and which are effective enough to justify the added cost of the modified grease composition. In the course of our studies, we have discovered that certain higher alkylated diphenylamine derivatives improve the oxidation stability of grease compositions. We have discovered moreover that the use of a small proportion of such a higher alkylated diphenylamine in combination with a small proportion of a dimethylaminomethyl alkylphenol is markedly superior to either material alone in imparting oxidation stability to lubricating greases. The ring substituted alkyl groups are high enough in molecular weight to contribute oil solubility. Thus we have found that dioctyl diphenylamine or mixed mono- and di-heptyl diphenylamine, for example, appears to cooperate synergistically with 2,6-di(dimethyl-aminomethyl)-4-octylphenol in inhibiting oxidation deterioration of lubricating greases.

We have found that only small proportions of each agent, e. g. about 0.05 to about 2 weight per cent, are required. Advantageously, about 0.25 to 1.0 per cent of the mixture is employed in equal proportions of each. The actual amount employed usually is varied according to the nature of the grease, its susceptibility to oxidation and the nature of the service for which it is intended. In manufacture, the materials are conveniently and usually added to the grease kettle in the finishing stages. The materials may be added as such or in the form of oil concentrates. We have found that the combination of the alkylated diphenylamine and the aminomethyl alkyl phenol has general effectiveness of a high order in grease manufacture. Thus the materials are compatible with and effective in inhibiting lubricating greases manufactured from any of the conventional mineral oils whether conventionally or solvent refined and with any of the conventional soaps such as the lithium, calcium, sodium, aluminum, or mixed soaps of stearic acid, 12-hydroxy stearic acid, tallow, hydrogenated fish oil, hydrogenated castor oil, and the like.

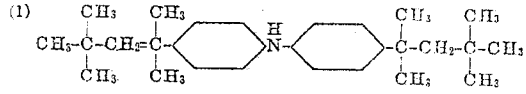
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We have no explanation for the particular mode of cooperation between the ingredients of our antioxidant combination. The structure of the alkylated diphenylamine may be represented as

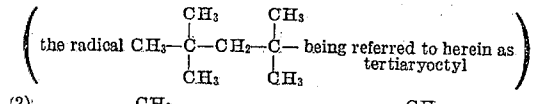


The alkyl groups R may be the same or different groups but should be high enough in molecular weight, e. g. hexyl, heptyl, octyl, nonyl, etc., to provide the necessary measure of oil solubility for incorporation in the grease compositions. Either of the ingredients may represent a single compound or may represent a mixture of compounds. In particular we have found the material sold commercially as octylated arylalkylated diphenylamine by the B. F. Goodrich Co. of special value in combination with an aminomethyl alkylphenol. This material is believed to represent the alkylation mixture produced by reaction of di-isobutylene, styrene and diphenylamine in the presence of a Friedel-Crafts catalyst as disclosed in U. S. Patent 2,530,769 to Arthur L. Hollis. As described in that patent, the reaction mixture comprises an oily composite which consists principally of the following compounds:

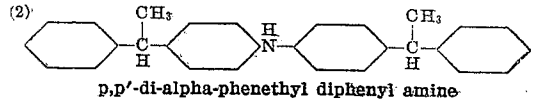
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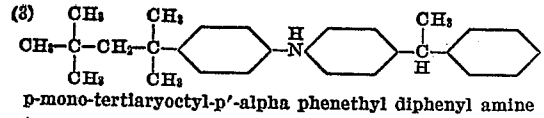
p,p'-di-tertiaryoctyl diphenylamine



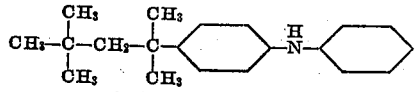
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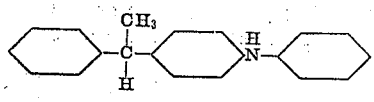
p,p'-di-alpha-phenethyl diphenyl amine

(3) 

p-mono-tertiaryoctyl-p'-alpha phenethyl diphenyl amine

(4) 

p-mono-tertiaryoctyl diphenyl amine

(5) 

p-alpha-phenethyl diphenyl amine

Compounds 1, 2 and 3 make up from 50 per cent to 70 per cent by weight of the product with compound 1 being most abundant of these, while compounds 4 and 5 make up the remaining 30 per cent to 50 per cent, with compound 4 being more abundant than compound 5.

The valuable aminomethyl alkyl phenols of our invention are represented by the materials known commercially as Hyamine A (DMP–10) and Hyamine B (DMP–14) and sold by the Rohm and Haas Company. To the best of our knowledge, these materials are respectively 2,6-di-(dimethylamino-methyl)-4-butylphenol and 2,6-di-(dimethyl-amino-methyl)-4-octylphenol. Similar amino-alkylated phenols having the requisite oil solubility are also effective.

The nature of our invention will be further illustrated by reference to the experimental data of the following examples. In the examples the test greases were conventionally manufactured by heating the fats and/or fatty acids in the presence of about 20 per cent of the oil, adding the alkali to effect saponification, continuing the heating with agitation until the reaction was complete and a smooth dehydrated mixture was obtained, and finishing by oil addition to the desired consistency. The oxidation data were obtained by application of the Norma-Hoffman oxidation test procedure, ASTM D 942–47 T. In addition an "induction period" is reported which indicates the elapse of time from the start of the test to the time when there is a very rapid drop of pressure. This point is considered to be the point of complete breakdown of resistance to oxidation which is followed by rapid absorption of the oxygen by the grease causing the subsequent pressure drop.

In the following tests, oxidation data were obtained on a number of Ang–5–A and 14–L–3c type greases. The greases comprised mixed sodium and calcium soaps of stabilized tallow and hydrogenated fish oil fatty acids combined with solvent treated mineral oils. Oxidation inhibitors of the kind and in the amounts indicated were incorporated in the greases as shown in the following table.

Concentration of Inhibitor	Induction Period	Pressure drop in pounds				
		100 Hrs.	200 Hrs.	300 Hrs.	400 Hrs.	500 Hrs.
None	60	80+				
0.25% DMP–10 [2,6-di-(dimethyl-aminomethyl)-4-butylphenol]	144	6	60+			
1.00% DMP–10		3	5	8	11	15
1.00% Mixed mono- and di-heptyl diphenylamine		6	11	15	17	20
0.5% Mixed mono- and di-heptyl diphenylamine and 0.5% DMP–10		3	6	7	10	11
0.25% Mixed mono- and di-heptyl diphenylamine and 0.25% DMP–10		5	6	8	10	12
0.10% Mixed mono- and di-heptyl diphenylamine and 0.10% DMP–10		2	5	8	10	12
0.50% DMP–14 [2,6-di-(dimethyl-amino-methyl)-4-octylphenol]	280	3	6			
1.00% DMP–14		4	6	8	9	11
0.50% Mixed mono- and di-heptyl diphenylamine and 0.50% DMP–14		3	5	7	8	9
0.50% DMP–14 and 0.50% octylated arylalkylated diphenylamine		4	6	9	10	12
0.50% DMP–10 and 0.50% Octylated arylalkylated diphenylamine		4	6	9	10	12
1.00% Dioctyl diphenylamine		7	14	19	22	26
0.50% DMP–14 and 0.50% Dioctyl diphenylamine		3	6	7	9	11

It will be noted that in each case the combination of inhibitors produced superior results to the use of either inhibitor alone and also permitted a reduction in the total quantity of inhibitor required without appreciable loss of effectiveness. Similar results have been obtained in tests on other type greases. For example a bearing AF type grease comprising mixed sodium and calcium soaps with hydrogenated fish oil fatty acids, beef tallow and tallow fatty acids combined with conventionally refined neutrals had an induction period alone of only 10 hours and after 100 hours under the Norma-Hoffman oxidation conditions showed a pressure drop of greater than 35 p. s. i. When inhibited with 0.25 per cent mixed mono and diheptyl diphenylamine and 0.25 per cent DMP–10, the following Norma-Hoffman oxidation were obtained:

Pressure drop in pounds				
100 Hrs.	200 Hrs.	300 Hrs.	400 Hrs.	500 Hrs.
3	5	8	12	14

Comparable results were obtained with a conventional sodium-tallow soap grease made with 90 to 95 viscosity at 210° F. conventionally refined oil. In addition we have checked a wide variety of commercially used greases, including all purpose greases of the type employing lithium soaps, and have found the combination of inhibitors of our invention peculiarly effective in improving the oxidation resistance of the greases.

We claim:

1. A grease composition consisting essentially of a mineral oil and soap compounded grease and about 0.05 to about 2 weight percent of an oil-soluble higher alkylated diphenylamine and about 0.05 to 2 weight percent of a dimethylaminomethyl alkylphenol.

2. The composition of claim 1 in which the dimethylaminomethyl alkylphenol is 2,6-di-(dimethylaminomethyl)-4-butylphenol.

3. The composition of claim 1 in which the dimethylaminomethyl alkylphenol is 2,6-di-(dimethylamino-methyl)-4-octylphenol.

4. The composition of claim 1 in which the alkylated diphenylamine is mixed mono- and diheptyl diphenylamine.

5. The composition of claim 1 in which the alkylated diphenylamine is octylated arylalkylated diphenylamine.

GEORGE ENTWISTLE.
HENRY JOHN VOSS.

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