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TRANSFORMER OIL COMPOSITION

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This invention relates to transformer oil compositions highly resistant to undesirable oxidation changes, and comprising petroleum oils containing in admixture therewith relatively small amounts of a combination of addition agents exceptionally useful in protecting said oils against oxidation and sludge formation.

Petroleum oils are widely used in electrical transformers, primarily for the purpose of dissipating heat from the windings to the transformer case, and also for the secondary purpose of electrical insulation. Such oils must possess sufficiently low viscosity to facilitate transfer of heat by convection, low pour point to prevent solidification of the oil at low temperatures, high flash and fire points to reduce danger of explosion and fire, low volatility in order to minimize evaporation losses, high dielectric strength, and resistance to oxidation, and must be of such character as to emulsify with water only with the greatest difficulty.

Petroleum oils used for this purpose ordinarily comprise distillate oils refined to such extent as to possess the characteristics noted above to as great an extent as is possible. However, these oils do undergo oxidation changes which result in the formation of insoluble matter or sludge. This is in turn undesirable not only because of the fact that sludge so formed tends to render the oil more susceptible to form emulsions in the presence of condensed water, but because the deposition of sludge on the windings of the transformer tends to reduce the efficiency of heat transfer. These oxidation changes, while slow, are nevertheless serious because of the fact that transformer oils are ordinarily employed over exceedingly long periods of time. Oxidation of the oil tends to be promoted by contact of the oil with metals (especially copper), varnishes and insulating materials, by catalysis or otherwise.

In determining the value of oils for use in transformers, some sort of accelerated oxidation test is ordinarily employed. One commonly used method of testing comprises subjecting the oil to contact with air or oxygen at moderately elevated temperatures in the presence of copper or other metal tending to increase the oxidation of the oil. The results of such tests are commonly evaluated both in terms of the so-called induction period, that is to say, the time which elapses prior to the appearance of sludge in the oil when subjected to the test, and in terms of the amount of sludge formed per day after the first appearance of sludge. The ultimate consideration must, of course, be the combined effect of these two

factors, which may conveniently be expressed as the time which elapses between the start of the test and the development of a fixed quantity, say 0.1 per cent, of sludge in the oil.

There are a number of substances which, when added to petroleum oils, tend to increase the induction period of the oil as measured by a test of the character indicated above, and there are other substances which tend to decrease the rate of sludge formation after the initial appearance of sludge. Since both factors are important and must be considered in order to determine the ultimate value of the compounded oil, there is need for a combination of agents which when added to petroleum oil will yield a compounded oil or composition having both a high induction period and a low rate of sludge formation per day; that is to say, an oil in which the length of time required to form a given amount of sludge, under accelerated conditions of oxidation, will be high.

Unfortunately, however, antioxidants of various types are not ordinarily cumulative in effect and the effect of a combination of antioxidants of various types cannot be predicted from consideration of the effects of the individual agents when these agents are added alone to petroleum oils.

I have found, however, that petroleum oils to which have been added relatively small amounts of diphenylamine and certain alkylated phenols possess exceptional utility as transformer oils and that when these agents are used in combination, the effect of the combination is from an over-all standpoint considerably better than could have been predicted from the behavior of the individual agents, when added alone. The total effect is not merely cumulative or additive.

Both of these types of compounds are of some value individually as antioxidants but combinations thereof are unpredictably efficient.

The alkylated phenols contemplated by my invention are alkylation products of phenols and substituted phenols, in which there are present alkylation linkages of secondary or preferably tertiary type. They do not include phenol itself or such alkyl substituted phenols as the cresols, xlenols and ethyl phenols themselves but they do include tertiary butyl, tertiary amyl and similar alkyl derivatives of such phenols, as well as similar derivatives of benzyl-substituted, cyclohexyl-substituted and other substituted phenols. The preferred members of the class contemplated are those in which at least one or both of the

tertiary or secondary alkyl groups is or are in a position ortho to the hydroxyl group.

The alkylated phenol which I prefer to employ, due to consideration of its effectiveness, ease of preparation, solubility in oil, insolubility in water and dilute alkali solution and cheapness, is 2,6-di-tertiary-butyl-4-methyl phenol. Other alkylated phenols which I have found useful include the following:

- 2,6-di-tertiary-butyl-4-ethyl-phenol
- 2,6-di-tertiary-butyl-4-cyclohexyl-phenol
- 2,6-di-tertiary-butyl-4-benzyl-phenol
- 2,4,6-tri-tertiary-butyl-phenol
- 2,6-di-tertiary-amyl-4-methyl-phenol

For the most part, such alkylated phenols are readily prepared by alkylating phenols or substituted phenols with olefins, such as isobutylene, under conditions favorable to promote alkylation, as for example under heat and pressure, in the presence of the usual acid condensing agents, or both. My invention, however, is not limited to any particular manner of preparing such alkyl phenols, as they may be prepared in various manners, and the particular method of preparation does not affect the activity of individual compounds so prepared.

In general, the amounts of such materials employed in accordance with my invention are not in excess of 1 per cent of the oil to be inhibited. I have found that 0.1 per cent by weight of diphenylamine is effective, but this may be varied in accordance with the results desired, although it should not ordinarily be necessary to employ more than 0.5 per cent of diphenylamine in any case. Similarly the amount of alkylated phenol employed is ordinarily somewhat larger than the amount of diphenylamine employed. I have used 0.3 per cent and 0.2 per cent by weight of the alkylated phenol with considerable success and it should not be ordinarily necessary to add more than 1 per cent, at the most, to any particular oil.

The oil bases to which these agents are added in admixture, in accordance with my present invention, are the usual transformer oils, ordinarily comprising highly refined petroleum distillates having physical characteristics within the ordinary specifications for transformer oil. Acid-refined and solvent-refined oils may be employed, and in some instances it is desirable to employ oils which have been subjected both to acid-refining and solvent-refining methods.

The following data will further serve to illustrate the application of my invention and utility thereof:

These test data were obtained in accordance with the sludge formation test for mineral transformer oil, described by F. M. Clark and E. A. Snyder in their paper entitled "Testing for sludge formation in mineral transformer oil" presented at the thirty-ninth annual meeting for the American Society for Testing Materials. The technical investigation described in the aforesaid paper was carried out in collaboration with the laboratories of a considerable number of firms engaged in oil refining and in the manufacture of electrical equipment.

Briefly, samples of oil are maintained in tubes containing copper wire at a constant temperature of approximately 120° C. The tubes are open at the top to an enclosed air space and dry air is passed at a controlled rate of 1½ to 2 cubic feet per hour through the enclosed space above the sample tubes. Into each tube is introduced 22 grams of oil of oil composition to be tested, a

number of tubes being employed. At prescribed intervals the tubes are successively removed and the amount of sludge determined. The results of these tests are reported in terms of the induction period, the per cent of sludge formed per day and the total number of days taken to form 0.1 per cent of sludge.

The oil employed in all of the tests set forth hereinbelow was a typical petroleum transformer oil, commonly used for the purpose indicated. The results obtained in testing the oil alone and in testing the oil together with both the individual addition agents and combinations thereof are as follows:

TABLE I

Run	Sample tested	Induction period, days	Rate of sludge formation, per cent per day	Total days to form 0.1% sludge
A	Oil base without addition agent.	0	0.0114	8.5
B	Same oil plus 0.3% of 2,6-di-tertiary-butyl-4-methyl phenol.	10	0.0250	14
C	Same oil plus 0.1% diphenylamine.	1	0.0110	10
D	Same oil plus 0.3% of 2,6-di-tertiary-butyl-4-methyl phenol plus 0.1% diphenylamine.	9.5	0.0080	23
E	Same oil plus 0.3% of 2,6-di-tertiary-butyl-4-ethyl-phenol.	8	0.0270	11.5
F	Same oil plus 0.3% of 2,6-di-tertiary-butyl-4-ethyl phenol plus 0.1% diphenylamine.	8	0.0055	26
G	Same oil plus 0.3% of 2,6-di-tertiary-butyl-4-cyclohexyl-phenol.	2	0.0110	11
H	Same oil plus 0.1% of 2,6-di-tertiary-butyl-4-cyclohexyl-phenol plus 0.1% diphenylamine.	2	0.0058	19.5
I	Same oil plus 0.3% of 2,6-di-tertiary-butyl-4-benzyl-phenol.	2	1.0100	13
J	Same oil plus 0.3% of 2,6-di-tertiary-butyl-4-benzyl-phenol plus 0.1% diphenylamine.	2	0.0030	34

It will be evident from the above that the combination of addition agents in accordance with my invention is far more effective, in terms of over-all effectiveness, than any of the individual agents considered alone. Thus, comparing the results obtained in runs A, B, C and D, it will be noted that the addition of 0.3 per cent of 2,6-di-tertiary-butyl-4-methylphenol increases the induction period from 0 to 10 days but more than doubles the rate of sludge formation thereafter, so that the total increase in the number of days required to from 0.1 per cent of sludge was only 5.5 days. The addition of 0.1 per cent of diphenylamine, on the other hand, increased the induction period only to one day and lowered the rate of sludge formation thereafter to a very slight extent only, thereby increasing the total days to form 0.1 per cent of sludge by only 1.5 days.

Whereas the alkylated phenol, as in run B, more than doubled the rate of sludge formation following the induction period, and the diphenylamine alone only very slightly decreased the formation of sludge, the combination of these two materials results in a very striking decrease in the rate of sludge formation, namely down to 0.0080 per cent per day. Consequently, the combination of the two addition agents, as shown in run D, increases the total days to from 0.1 per cent of sludge from 8.5 to 23 days, an increase of 14.5 days as compared with 5.5 days and 1.5 days for

the individual addition agents when employed alone. These results clearly indicate that these two agents are far more effective when employed in combination with each other than when employed alone.

Similarly the results reported under runs E to J, inclusive, demonstrate similarly striking and valuable results in favor of other types of alkylated phenols of the class defined herein, used in combination with diphenylamine.

Other tests conducted on similar oil compositions within the scope of my invention have shown that the oil compositions of my invention are also effective in reducing the deterioration of transformer insulating tape. The results given in the following table are typical of these tests.

TABLE II

*Effect of transformer oils on insulating tape,
95 hrs., 200° F.*

Oil	Gain in weight of tape, percent	Neut. No. of oil	Color of oil, N. P. A.
Transformer oil alone.	6.3	0.46	4½
Same transformer oil plus 0.3% of 2,6-di-tertiary-butyl-4-methyl-phenol plus 0.1% diphenylamine.	3.9	0.20	2

It will be obvious to those skilled in the art that my invention is not limited to the specific examples given hereinabove by way of illustration and exemplification, but may be variously practiced and embodied within the scope of the claims hereinafter made.

What I claim is:

1. A transformer oil comprising a petroleum oil, normally subject to oxidational deterioration resulting in the formation of sludge, having in admixture therewith relatively small amounts of diphenylamine and a secondary or tertiary alkyl phenol, the amounts of said last-mentioned agents present being sufficient at least to substantially retard sludge formation.

2. A transformer oil comprising a petroleum oil, normally subject to oxidational deterioration resulting in the formation of sludge, having in admixture therewith relatively small amounts of diphenylamine and a secondary or tertiary alkyl-substituted cresol, the amounts of said last-mentioned agents present being sufficient at least to substantially retard sludge formation.

3. A transformer oil comprising a petroleum oil, normally subject to oxidational deterioration resulting in the formation of sludge, having in admixture therewith relatively small amounts of diphenylamine and a secondary or tertiary alkyl-substituted and benzyl-substituted phenol, the

amounts of said last-mentioned agents present being sufficient at least to substantially retard sludge formation.

4. A transformer oil comprising a petroleum oil, normally subject to oxidational deterioration resulting in the formation of sludge, having in admixture therewith relatively small amounts of diphenylamine and a secondary or tertiary alkyl-substituted and cyclohexyl-substituted phenol, the amounts of said last-mentioned agents present being sufficient at least to substantially retard sludge formation.

5. A transformer oil comprising a petroleum oil, normally subject to oxidational deterioration resulting in the formation of sludge, having in admixture therewith relatively small amounts of diphenylamine and a secondary or tertiary alkyl-substituted phenol, wherein at least one of the secondary or tertiary alkyl groups occupies a position ortho to the hydroxy group, the amounts of said last-mentioned agents present being sufficient at least to substantially retard sludge formation.

6. A transformer oil comprising a petroleum oil, normally subject to oxidational deterioration resulting in the formation of sludge, having in admixture therewith relatively small amounts of diphenylamine and 2,6-di-tertiary-butyl-4-methyl phenol, the amounts of said last-mentioned agents present being sufficient at least to substantially retard sludge formation.

7. A transformer oil comprising a petroleum oil, normally subject to oxidational deterioration resulting in the formation of sludge, having in admixture therewith relatively small amounts of diphenylamine and 2,6-di-tertiary-butyl-4-cyclohexyl phenol, the amounts of said last-mentioned agents present being sufficient at least to substantially retard sludge formation.

8. A transformer oil comprising a petroleum oil, normally subject to oxidational deterioration resulting in the formation of sludge, having in admixture therewith relatively small amounts of diphenylamine and 2,6-di-tertiary-butyl-4-benzyl phenol, the amounts of said last-mentioned agents present being sufficient at least to substantially retard sludge formation.

9. A transformer oil comprising a petroleum oil, normally subject to oxidational deterioration resulting in the formation of sludge, having in admixture therewith about 0.3 per cent of 2,6-di-tertiary-butyl-4-methyl phenol and about 0.1 per cent of diphenylamine, said last-mentioned agents being effective in combination both to retard the appearance of oxidational sludge in the oil and the rate of sludge formation thereafter.

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