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INSULATING OIL COMPOSITION

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This invention relates to improved insulating oil compositions and it comprises improved transformer oils and other insulating oil compositions, highly resistant to undesirable oxidational changes, said improved oil compositions comprising a major amount of petroleum oil containing in admixture therewith relatively small amounts of 2,6-di-tertiary-butyl-4-methyl phenol and of trithiophenyl phosphate, as improvement agents, the total amount of the combined improvement agents being sufficient to stabilize the petroleum oil against oxidation, particularly against sludge formation, development of acidity and other undesirable changes normally resulting from oxidation of the oil under service conditions and to otherwise improve said oil compositions; all as more fully hereinafter set forth and as claimed.

In the present invention transformer oils and like insulating oils are markedly improved by incorporating in the oil a small amount of a particular combination of improvement agents, namely, trithiophenyl phosphate and 2,6-di-tertiary-butyl-4-methyl phenol; the amount of this combination of agents added to the oil being sufficient to stabilize the oil against oxidation, as stated ante. And the total amount of such additions necessary to effectively stabilize the usual commercial oils does not exceed 1 per cent by weight on the oil. For instance, by adding 0.1 to 0.3 per cent of trithiophenyl phosphate and 0.1 to 0.3 per cent 2,6-di-tertiary-butyl-4-methyl phenol to transformer oil, I have obtained oil compositions which are very stable against oxidation.

The improved oils so obtained are exceptionally resistant to sludging and this is due to the cooperative actions of the two agents present in the oil, as more fully shown post. And as there shown, my new and improved oils, in addition to being vastly superior to the original oils, are also superior to oils containing only one of these agents in comparable amounts. And my new oil compositions because of their superior resistance to oxidation and other improved properties possess exceptional utility as transformer oils.

In many types of electrical transformers the core and windings are immersed in a suitable petroleum oil, which serves as a dielectric and for carrying heat away from the core and windings. The requirements of a transformer oil include good dielectric properties, low viscosity to facilitate heat transfer by convection, low pour point to avoid solidification of the oil by cold, high flash and fire points to minimize danger of fire and explosion and low volatility to reduce evaporation losses. In addition the oil must be resistant to oxidation and sludging, and must be of such character as to resist emulsification with water.

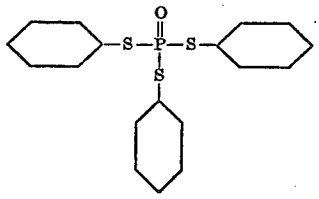
Transformer oils ordinarily are distillate oils refined in such manner as to secure the specified characteristics to as great an extent as possible. Achievement of satisfactory oxidation resistance is difficult, for while oxidational changes are slow, transformer oils are ordinarily expected to remain in service over long periods. Oxidational changes result in the formation of insoluble matter or sludge. The sludge tends to render the oil more miscible with water, with production of emulsions in the presence of condensed water and a consequent degradation of the dielectric properties of the oil body. The sludge also deposits on the windings and core with reduction of the efficiency of heat transfer. Oxidation of transformer oils tends to be promoted by contact with metals, especially copper, and with the usual varnishes and insulating materials.

Various materials have been proposed for incorporation into transformer oils with the object of inhibiting oxidation, and some of these have come into use. The usual anti-oxidants may be divided in two principal classes: (1) those which are associated with a lengthening of the induction period, that is the time which elapses before appearance of sludge in the oil subject to oxidation, and (2) those which reduce the rate of sludge formation after it once begins to form. In evaluating oils containing anti-oxidants, the most useful criterion is a value which takes into account both these characteristics, viz., the time required, under the test conditions, to form a definite amount of sludge, say 0.1 per cent by weight of the oil.

The 2,4,6-tri-alkylated monohydroxy phenols having four or more carbon atoms in the alkyl groups ortho to the hydroxyl group which are substantially insoluble in water and in dilute aqueous alkali, have proved particularly satisfactory as antioxidants in transformer oils in lengthening the induction period before sludge begins to form. The compound 2,6-di-tertiary-butyl-4-methyl phenol is quite effective for this purpose. It has been found however that after the induction period in a transformer oil containing a compound of this class, the rate of sludge formation is sometimes greater than in the original oil. Thus the total time required to form 0.1 per cent of sludge in the oil is often shorter than would be expected in view of the prolonged induction period.

I have discovered that this difficulty can be

overcome by incorporating in a transformer oil along with the 2,6-di-tertiary-butyl-4-methyl phenol, a small amount of trithiophenyl phosphate having the formula:



I have found that a transformer oil composition thus produced has an extraordinarily low rate of sludge formation in addition to a long induction period so that the useful life of the oil is substantially increased. The trithiophenyl phosphate modifies the action of the 2,6-di-tertiary-butyl-4-methyl phenol during the induction period and the sludge forming rate after the induction period is lower than is obtainable with either of these antioxidants alone. Only very small amounts of trithiophenyl phosphate are required to effectively stabilize transformer oils containing 2,6-di-tertiary-butyl-4-methyl phenol.

In preparing my improved transformer oils, the amounts of these improvement agents added to the oil are advantageously less than 1 per cent by weight on the oil to be inhibited. I have found that from 0.1 to 0.3 per cent by weight of trithiophenyl phosphate and 0.1 to 0.3 per cent by weight of 2,6-di-tertiary-butyl-4-methyl phenol in combination are effective with most transformer oils. Of course the exact amounts required vary with the particular oil employed and the exact amounts used may be varied within the stated range to give the stability and other improvements desired with any particular oil. Ordinarily it should not be necessary to add more than 1 per cent of the combined agents to any particular oil.

The oil bases to which these agents are added in admixture, in accordance with the present invention, are the usual transformer oils ordinarily comprising highly refined petroleum distillates having the physical characteristics within the ordinary specifications for transformer oil. The 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 data given in the table post will serve to illustrate the application of my invention and the utility thereof. The test data given in the table were obtained in accordance with the sludge formation test for mineral transformer oil, described by F. M. Clark and E. A. Synder in their paper entitled "Testing for Sludge Formations in Mineral Transformer Oil," presented at the thirty-ninth annual meeting for the American Society for Testing Materials.

In the tests reported in said table, samples of oil and of the compounded oils were maintained in tubes containing copper wire at a constant temperature of 120° C. The tubes were opened at the top to an enclosed air space and dry air was passed at a controlled rate of 1½ to 2 cubic feet per hour through the enclosed space above the sample tubes. In each tube was introduced 22 grams of oil or oil composition to be tested, a number of tubes being employed. At prescribed intervals the tubes were 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 after the induction period and the total number of days required to form 0.1 per cent of sludge.

The oil employed in all of the tests set forth herein below 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 separately and combinations thereof are as follows:

Table I

No.	Transformer oil: Composition: Oil	Transformer oil: Composition: D-T-B. M. phenol	Transformer oil: Composition: T. T. P. phosphate	Induction period	Rate of sludge formation, after induction period	Total time to form 0.1 per cent sludge
	Parts	*Parts*	*Parts*	*Days*	*Per cent per day*	*Days*
1	100	----------	----------	0.5	0.0100	10
2	99.7	0.3	----------	12.5	0.0205	18
3	99.9	----------	0.1	1.5	0.0085	14
4	99.7	----------	0.3	3.0	0.0065	22
5	99.5	----------	0.5	6.0	0.0060	28
6	99.6	0.3	0.1	24.0	0.0063	36
7	99.4	0.3	0.3	30.0	0.0050	52

In the above table, the "Parts" are parts by weight and the abbreviations "D-T-B. M. phenol" and "T. T. P. phosphate" represent 2,6-di-tertiary-butyl-4-methyl phenol and trithiophenyl phosphate, respectively.

From the data given in the above table, it is evident that my improved transformer oils containing a combination of trithiophenyl phosphate and 2,6-di-tertiary-butyl-4-methyl phenol are vastly superior to the original transformer oil. Likewise, they are much superior to the same oil containing either one of these improvement agents alone, both in terms of the increased induction period and of the decreased rate of sludge formation thereafter, as well as in terms of over-all effectiveness.

Thus exceptional improvements are obtained by adding this particular combination of improvement agents to the transformer oil. The several improvements obtained by the present invention are apparent when the results obtained with the transformer oils Nos. 1 to 7 are compared.

By comparing the results obtained with the original oil No. 1 against those obtained with the transformer oils Nos. 6 and 7, made in accordance with the present invention, it will be seen that my improved transformer oils are much more stable against sludging than the original oil. For one thing, my improved oils have an induction period which is from 48 to 60 times greater than that of the original oil. Also, their rate of sludge formation after the induction period is even less than that of the original oil. Further, the total time to form 0.1 per cent sludge shows the over-all superiority of my improved compounded transformer oils over the original oil.

Likewise, by comparing the results obtained with my improved oils Nos. 6 and 7 against those obtained with oils Nos. 2 to 5, inclusive, the superiority of my improved oils over those containing only one of these agents is also apparent. And from the data given, it is evident that the improvements in resistance to sludging etc. obtained with my combination of improvement agents are much greater than would have been obtained had the effect of these improvement agents been merely cumulative. And the exceptional improvements obtained by adding my par-

ticular combination of improvement agents to the transformer oil are clearly shown by the data given ante. As to this it should be observed that my improved transformer oils have an exceptionally long induction period and an exceptionally low rate of sludge formation after the induction period, as compared with the transformer oils containing only one of these improvement agents.

While my invention has been described herein with particular reference to transformer oil compositions, the combination of trithiophenyl phosphate and 2,6-di-tertiary-butyl-4-methyl phenol is equally effective in stabilizing other electrical insulating oils against oxidational deterioration. And in addition to improving transformer oils, I can also improve other insulating oils by the present invention. In improving insulating oils generally, I likewise incorporate small amounts of my combination of improvement agents in the oil. The amount added to the oil may be varied according to the particular insulating oil employed to obtain the improvement desired. By the present invention, various types of insulating oils, such as cable oils, switch oils, circuit breaker oils, etc., as well as transformer oils, may be improved by incorporating sufficient of my combination of improvement agents in the oil to render it highly resistant to sludging and other deleterious oxidational changes under service conditions, without deleteriously affecting the electrical and physical properties of the oil necessary for the various uses thereof as a dielectric or insulation media.

What I claim is:

1. As a new and improved transformer oil, a transformer oil containing in admixture therewith relatively small amounts of trithiophenyl phosphate and of 2,6-di-tertiary-butyl-4-methyl phenol, the said improved transformer oil being highly resistant to sludging and to other oxidational deterioration under service conditions and the amount of such combination of improvement agents being less than 1 per cent.

2. In the manufacture of improved insulating oils, the improved process which comprises incorporating relatively small amounts of trithiophenyl phosphate and of 2,6-di-tertiary-butyl-4-methyl phenol in a petroleum oil normally subject to oxidational deterioration resulting in the formation of sludge, the amount of such combination of improvement agents being less than 1 per cent and being sufficient to render said petroleum oil highly resistant to sludging and other oxidational deterioration under service conditions.

3. The process of claim 2 wherein said oil is a transformer oil.

4. As a new and improved insulating oil, an insulating oil comprising a petroleum oil having in admixture therewith relatively small amounts of trithiophenyl phosphate and of 2,6-di-tertiary-butyl-4-methyl phenol, said petroleum oil being normally subject to oxidational deterioration resulting in the formation of sludge, and the amount of said improvement agents being less than 1 per cent and being sufficient to substantially retard sludge formation and other oxidational deterioration.

5. A new and improved transformer oil comprising a petroleum oil having incorporated therein from 0.1 to 0.3 per cent of trithiophenyl phosphate and from 0.1 to 0.3 per cent of 2,6-di-tertiary-butyl-4-methyl phenol, the said improved transformer oil being highly resistant to sludging and to other oxidational deterioration under conditions normally obtaining in use.

6. In the operation of electrical transformers containing a petroleum oil as the dielectric and cooling medium, the improvement which comprises insulating and cooling the windings and core of the transformer with a petroleum oil containing in admixture therewith relatively small amounts of trithiophenyl phosphate and of 2,6-di-tertiary-butyl-4-methyl phenol.

7. The process of claim 6 wherein said petroleum oil contains in admixture therewith from 0.1 to 0.3 per cent of trithiophenyl phosphate and from 0.1 to 0.3 per cent of 2,6-di-tertiary-butyl-4-methyl phenol.

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