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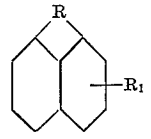
INSULATING OIL COMPOSITIONS CONTAINING ACENAPHTHENE OR ACENAPHTHYLENE

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ABSTRACT OF THE DISCLOSURE

Novel insulating oil compositions comprising a mineral insulating oil in major amount and a minor amount of a cyclic hydrocarbon having the formula:



wherein an R is a bivalent radical, i.e., —CH=CH— or —CH_2—CH(R_1)—, and R_1 is hydrogen, alkyl, or aryl, the alkyl and aryl ranging from C_1 to C_{12}.

The present invention relates to the preparation of novel insulating oil compositions wherein certain additives are employed for the purpose of reducing the tendency of such oils in service to form gases and, at the same time, having these oils possess marked tendencies toward minimizing oxidation and thus having improved stability. These insulating oils are generally employed in transformers, condensers, and in filled or hollow electrical cables.

The non-gassing characteristics and the oxidation stability of insulating oils depend, in large degree, upon the types of mineral oils employed and from which certain cuts or distillate fractions are isolated. Also, they depend upon what additives, if any, are employed in connection with compounding such oils for special purposes or for use under specialized conditions. For the most part, the insulating oils are employed as transformer oils. They must possess the ability to maintain high dielectric or insulating strengths within the transformers. They must remain relatively stable to oxidation and degradation. In addition, once they are degassed immediately prior to service, they should possess a minimum tendency toward the formation of additional quantities of gas while in service. Transformer oils are well known and have been used in the past in great quantities for said purposes. The petroleum crude oils from which such transformer oil fractions are derived may be of paraffinic, naphthenic, asphaltic, or mixtures of two or more of these three types of crude oils. In any event, such oils, in order to possess high dielectric properties, are necessarily subjected to rather sophisticated refining treatments for the purpose of improving their dielectric properties and oxidation stability.

It will at once be appreciated that excessive gassing of transformer or cable oils in service is hazardous both from the standpoint of permitting the equipment to breakdown and also from the standpoint of build-up of gas pressure which can cause rupture of the transformer containers or of the cable sheaths due to gas explosion. Many of the oils commercially marketed as cable and

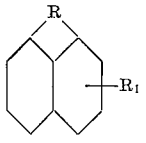
transformer oils now meet minimum dielectric properties, have good heat transfer properties, and are relatively stable insofar as oxidation breakdown is concerned. In many instances, however, it has been difficult to find such oils because of the high stresses encountered in present day transformers and cables. Such oils now must possess high resistance to gassing during service. Not only is there a tendency for possible explosion to occur where large amounts of gas are formed during use of the oils but also, even if an explosion or rupture of the casing does not occur, the gas will form pockets within the transformers or cable sheaths and thus remove the insulating oil medium from its critical areas where it is required thus losing its dielectric utility as well as its heat conducting properties at those spots. This results in uneven heat removal and in possible hazardous short circuiting of the transformer elements or cable conductors. Ordinary transformer oils are carefully degassed by conventional methods just prior to being placed in service. Particularly in transformers having outputs or ratings of 735,000 volts and having presently projected ratings of 1,000,000 volts, the dielectric stresses are or will be even more rigorous than has heretofore been encountered.

It is therefore apparent that some method of minimizing gas formation during service is necessary for those oils which will be used in connection with transformers and cables presently being designed or just recently having been placed in service having voltage ratings of 700,000 to 1,000,000 volts. Extensive studies were undertaken in an attempt to arrive at such suitable compositions and, while many types of compounds were investigated, only a very specific type of compound was found to be satisfactory. Thus, compounds such as fluorene, tetralin, indene, tetramethyl benzene (durene), 5-tertiary meta-xylene, α- or β-dodecyl naphthylene, and the like, have beeen found to be unsuitable as additives because they are either too volatile and are readily vaporized from the composition and thus their effectiveness lost, or they are too readily oxidized. In some cases these additives were unsuitable for both reasons.

It has been discovered, however, that certain types of cyclic hydrocarbons are especially beneficial, in amounts ranging between about 0.5% and about 20% or even more, if desired, based on the total weight of the composition, when added to such insulating oils. The insulating oils into which such additives are incorporated are those which are commercially marketed in the United States, Canada, and throughout the world. By and large, these oils are of naphthenic and/or paraffinic petroleum origin. Suitable oils are, for example, derived from naphthenic coastal distillates or from naphthenic TiaJuana crudes. Many of these oils are not wholly naphthenic or paraffinic in nature but are what is best described as being of mixed crude origin and, in many instances, they will contain from 5 up to as high as 35% aromatic hydrocarbon content. The saturated oils generally have a greater tendency to gas then do those oils containing appreciable amounts of certain types of aromatics. The novel additives hereinafter more fully discussed, imparting the non-gassing characteristics to the insulating oils while maintaining superior oxidation stability, particularly so in connection with those saturated oils which have a minimum content of aromatics, i.e., no more than 20% aromatics, are advantageous for still another reason. One drawback to using highly aromatic insulating oils is that they possess higher density generally than do the naphthenic or paraffinic oils devoid of or containing small

amounts of aromatics. This precludes their use at low ambient temperatures because of the tendency of ice to form in the bottom of the transformers and which then tends to float in these denser oils.

The novel compounds which are added in the aforementioned amounts to the various type of insulating oils are best represented by the formula:



wherein R is a bivalent radical, i.e., —CH=CH—, or —CH_2—CH(R_1)—, and R_1 is hydrogen, alkyl, or aryl, the alkyl and aryl ranging from C_1 to C_{12}. Representative examples of specific compounds coming within the scope of this class of compounds are the following: acenaphthene, acenaphthylene, 1-methyl acenaphthene, 1-dodecyl acenaphthene, 3-tetrapropylene acenaphthene, 3-ethyl acenaphthene, 1-n-butyl acenaphthene, 1-methyl acenaphthylene, 1-dodecyl acenaphthylene, 3-hexyl acenaphthylene, 1-phenyl acenaphthene, and 3-phenyl acenaphthene. In its simple form, the above formula embodies acenaphthene and acenaphthylene where R_1 is hydrogen. The substitution of alkyl radicals at either the 1-position or 3-position of the nucleus is best accomplished by conventional alkylation means involving the use of a mono-olefin or an alkyl or aryl halide such as the corresponding alkyl chloride or aryl (phenyl)chloride while employing an organic solvent and a catalyst such as aluminum chloride, BF_3, or some other conventional Friedel-Craft's type catalyst. Such processes are well known and conventionally used. In the case of the use of mono-olefinic polymers of C_{12} or lower such as tetrapropylene, these materials are available commercially and they may be either used directly as the alkylating agent or they may be mildly chlorinated and used as the corresponding alkyl chlorides for alkylating the cyclic hydrocarbon.

The cyclic hydrocarbon additives are used in amounts ranging between about 0.5 and about 20.0 wt. percent, preferably between about 1% and about 10 wt. percent, based on the total weight of the oil composition.

Inspections of typical oils available as insulating oils are shown in the following table:

TABLE I

Oil source	Pour point, ° F.	Viscosity at 100° F. (SUS)[1]	Flash point cleveland open cup. ° F.
A. Phenol treated hydrofined-naphthenic distillate (15% aromatic content)	−60	60	310
B. Hydrofined naphthenic Coastal distillate	−70	60	302
C. Caustic treated naphthenic Coastal Coastal distillate	(2)	58	284
D. Acid treated naphthenic Coastal distillate	(3)	60	(4)
E. Phenol extracted, dewaxed, hydrofined, paraffinic distillate (13% aromatic content)	−50	57	330
F. Naphthenic distillate, hydrogen treated (13% aromatic content)	−60	56	320

[1] Saybolt Universal Seconds.
[2] Below −22.
[3] Below −40.
[4] Above 302.

A number of tests were carried out in order to determine the properties of the various base oils and the novel compounded base oils for use as insulating oils. An examination of the same oils with and without the novel additives also were carried out to measure the oxidation characteristics and gassing rates of these same insulating oils. These tests were the bomb sludge test (ASTM D–1313–54), the modified Continental oxidation test, and the sludge accumulation test (ASTM D–1314–54T). The dielectric test used was ASTM D–877–49. In all instances, in view of the fact that the dielectric strength test was carried out at 30,00 volts and no higher, all oils without the additive and all oils with the additives shown hereinafter passed the dielectric tests.

The modified continental oxidation test was carried out in a Sligh oxidation flask equipped with ground glass joints. The procedure for the test was to introduce 13 ml. of insulating oil into the flask, submerging five clean strips of copper wire (2 inches in length) in the oil, as a catalyst, filling the entire free space of the flask with oxygen and immediately attaching to this a simple manometer (pressure indicating device). The manometer can be either of the mercury type or of the recording variety such as the Dickson pressure recording instrument. This entire assembly (except the pressure indicating device) is then placed in a constant temperature bath maintained at 115° C. (239° F.). The flask was allowed to come to equilibrium during ½ hour after introduction to the bath; after which time the oxygen pressure was recorded on the manometer. The test carried out measured the loss in pressure (or pressure drop) at intervals of 4 hours. The particular oils to pass this test must show a drop of less than 60 mm. pressure in 60 hours. Except for the fact that 13 ml. of oil was charged instead of 100 ml. and that the temperature was 115° C. instead of 120° C., this test is identical to the procedure described in ASTM Bulletin, pp. 65–74 (1947) authored by Leo J. Berberich.

Additionally, a series of gas formation experiments were undertaken on both the base oils used and as modified by the addition of varying amounts of cyclic hydrocarbons hereinafter shown. These gassing experiments were carried out using the Anaconda modification of the Pirelli cell and were carried out in the following manner:

About 15 cc. of the test insulating oil preheated to about 85° C. is placed in a modified Pirelli test cell immersed in an oil both maintained thermostatically at the same temperature of about 85° C. The cell is evacuated for 5 minutes at about 100 microns, or better, of mercury pressure (vacuum) after which nitrogen is introduced. The nitrogen gas is permitted to bubble through the oil sample for about 30 minutes to saturate the oil with the gas. The oil-gas interfaces is then subjected to an electrical stress of about 16,000 volts at 85° C. The rate of gas absorption or evolution is determined by recording the changes in gas volume above the oil-gas interface. The outer electrode of the cell is formed by a transparent conductive coating over the outer glass cylinder, which permits the observation of the gassing process. The lower part of the coating is metallized to permit good contact with the ground wire and the inner electrode is formed by filling the inner glass cylinder with a low melt point metal such as Cerroseal 35 or its equivalent.

Cerroseal 35 is a 50-50 mixture of indium and tin. In all cases, the oils under test showed either a zero reading as to gas or an evolution of gas. In no instances was there a gas absorption. See Table II of Example 1. Further details concerning the construction and arrangement of the Pirelli cell are disclosed in the paper presented by G. Palandri and U. Pelagatti at the 1954 convention of the Associazione Elettrotecnica, Italiana, Bellagio, Italy, Oct. 3–10, 1954, as to the use of the original Pireli cell and the paper presented to the conference on Electrical Insulation of the National Research Council, Pocono Manor, Pa. on Oct. 26–28, 1959 as to the modified Pirelli cell and procedure for using the same as heretofore described. This last mentioned paper is authored by G. Ferik, W. F. Olds, and E. D. Eich and is entitled, "The Gassing Properties of Low-Viscosity Cable Oils."

EXAMPLE 1

The gas formation test previously described (modified Pirelli cell) was carried out while employing the transformer oils as heretofore designated. The test was carried out at 85° C. oil temperature using 16,000 volts and varying amounts of acenaphthene (or 1.0% of acenaphthy-

lene) were added to the base oils with the rate of gas formation being measured in terms of microliters per minute (cc. per minute times 100). Nitrogen was used as the saturating gas in all tests. The following data were obtained:

TABLE II

Oil:	Gassing rate [1]
A	8.4
A+0.5% acenaphthene	7.9
A+0.1% acenaphthene	3.8
A+1.0% acenaphthylene	0.0
A+1.5% acenaphthene	1.75
E	13.6
E+1% acenaphthene	2.1
F	14.8
F+1% acenaphthene	7.1
F+2.0% acenaphthene	6.3

[1] Microliters per minute.

From a consideration of the above data, it is readily apparent that on a comparative basis, when using at least as much as 1% acenaphthene or acenaphthylene, a marked reduction in gassing rate was effected as compared with the gassing rate of the corresponding unmodified insulating oils. In general, it is desirable to secure a gassing rate not exceeding 5 microliters per minute. For this reason, for most types of service, the hydrocarbon treated oil F+1% acenaphthene which gave 7.1 microliters per minute of gassing would be unsatisfactory and would require a higher concentration (3.0%) of acenaphthene in order to give dependable service.

EXAMPLE 2

A further series of tests were carried out to establish the comparative oxidation stability of the base oils and the compounded base oils.

The following table sets forth the data obtained as a result of carrying out the various oxidation tests in the manner previously described.

TABLE III.—OXIDATION TESTS

Oil	Bomb sludge,[1] weight percent of oil	Modified continental after 60 hours, pressure drop, mm. Hg	Sludge accumulation test [2] after 36 hours: Weight percent sludge	Interfacial tension, dynes/cm.	Acid No. mg. KOH/gm. oil
A	.019	72	.31	16	.73
A plus 1% acenaphthene	.012	59	.30	13	.73
E	.031	47	.26	14	.95
E plus 1% acenaphthene	.023	52	.26	14	.70
F	.019	82			
F plus 1% acenaphthene	.018	66+			

[1] ASTM D-1313-54.
[2] ASTM D-1314-54T.

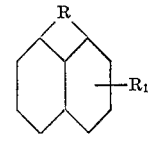
The above data show three oxidation tests: (a) the bomb sludge test (ASTM D-1313-54), (b) the modified Continental test (as previously described), and (c) the sludge accumulation test (ASTM-D-1314-54T). Additionally, the oils recovered after completion of the sludge accumulation test, in each instance, were subjected to an interfacial tension test and the acid number of these used oils was also determined. In both of these tests, the data obtained give some indication of the amount of oxidation which took place during the sludge accumulation test. An oil not previously subjected to the sludge accumulation oxidation test will ordinarily show an interfacial tension of more than 40 dynes per centimeter and likewise it will have an acid number of about 0.03.

Although the interfacial tension test is considered of less importance by many skilled in the art than the other tests shown in Table III, all of the data shown in Table III clearly indicate that the addition of 1% acenaphthene to the base transformer oils therein employed resulted in no appreciable increase in either the amount or the rate of oxidation of the compounded oil versus the uncompounded oil and in some cases, for example, the bomb sludge test, the amount of sludge formed was considerably less than that obtained in the case of the uncompounded oil. The acid number obtained was either less or no greater than that obtained in the case of the base oil alone. It is therefore apparent that, whereas, in Table II, the addition of the novel cyclic hydrocarbons to the base insulating oils resulted in a marked reduction in the amount of gassing obtained; this desirable goal was achieved without sacrificing, appreciably, the ability of the so compounded oils to resist oxidation degradation.

Having set forth the general nature and specific embodiments of the present invention, the true scope is now particularly pointed out in the appended claims.

What is claimed is:

1. An insulating oil composition comprising a major proportion of a mineral insulating oil having a flash point above 275° F. and a viscosity of less than about 75 SUS at 100° F. and a minor proportion of a cyclic hydrocarbon having the formula:



wherein R is a bivalent radical selected from the group consisting of —CH=CH— and —CH_2—CH(R_1)— and R_1 is a monovalent radical selected from the group consisting of H, C_1–C_{12} alkyl, and C_6 and C_{10} aryl.

2. A composition as in claim 1 wherein the cyclic hydrocarbon is acenaphthene.

3. A composition as in claim 1 wherein the cyclic hydrocarbon is acenaphthylene.

4. A composition as in claim 1 wherein the cyclic hydrocarbon constitutes between about 0.5 and about 20 wt. percent of the composition.

5. A composition as in claim 4 wherein the cyclic hydrocarbon is acenaphthene.

6. A composition as in claim 4 wherein the cyclic hydrocarbon is acenaphthylene.

7. A composition as in claim 5 wherein the acenaphthene is present in an amount between about 1 and about 10 wt. percent.

8. A composition as in claim 6 wherein the acenaphthylene is present in an amount between about 1 and about 10 wt. percent.

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