June 6, 1961 H. B. SKEES ET AL 2,987,536

OXIDATION PROCESS

Filed June 13, 1958 3 Sheets-Sheet 1

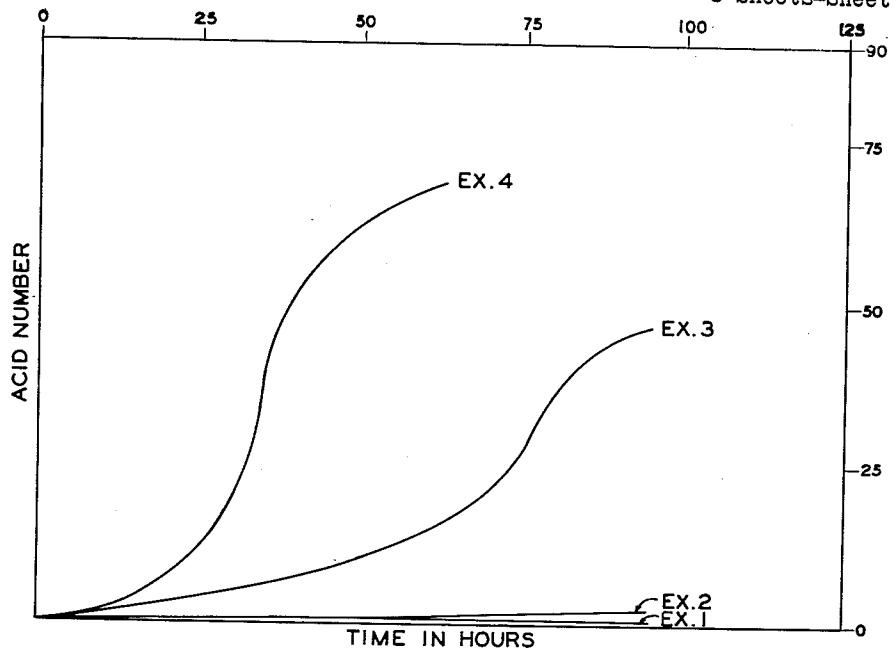


FIGURE 1

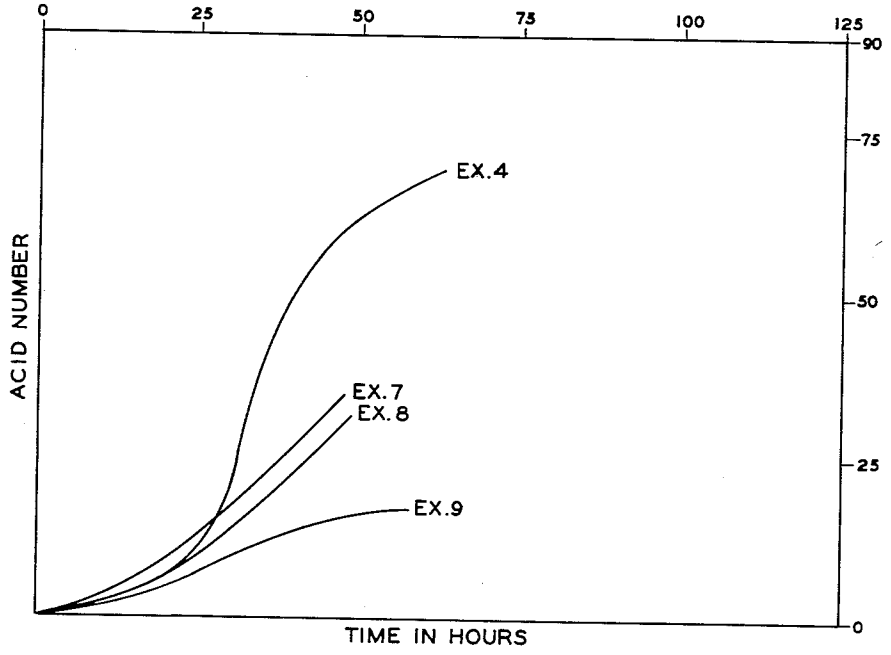


FIGURE 2

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OXIDATION PROCESS

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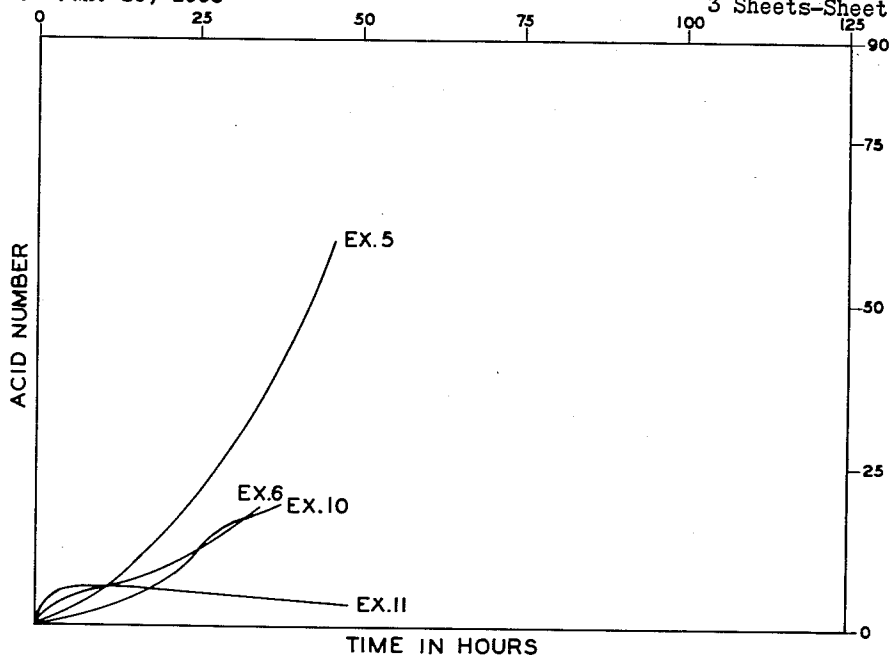


FIGURE 3

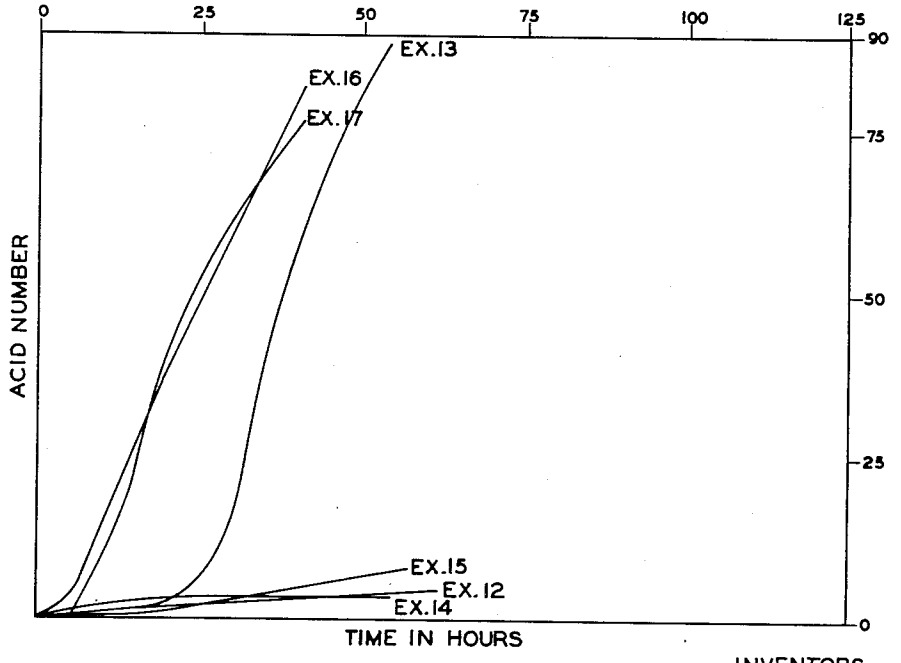


FIGURE 4

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OXIDATION PROCESS

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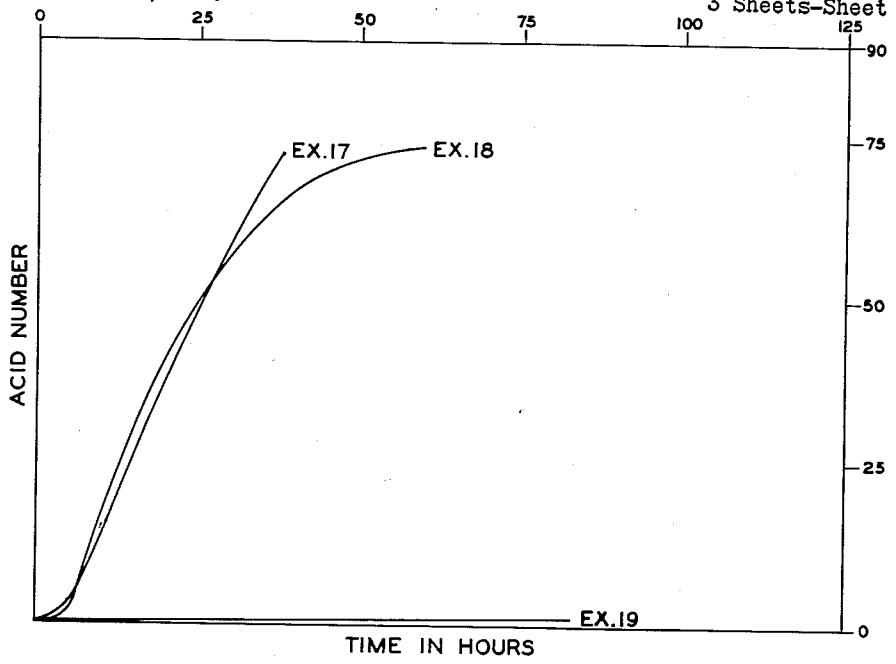


FIGURE 5

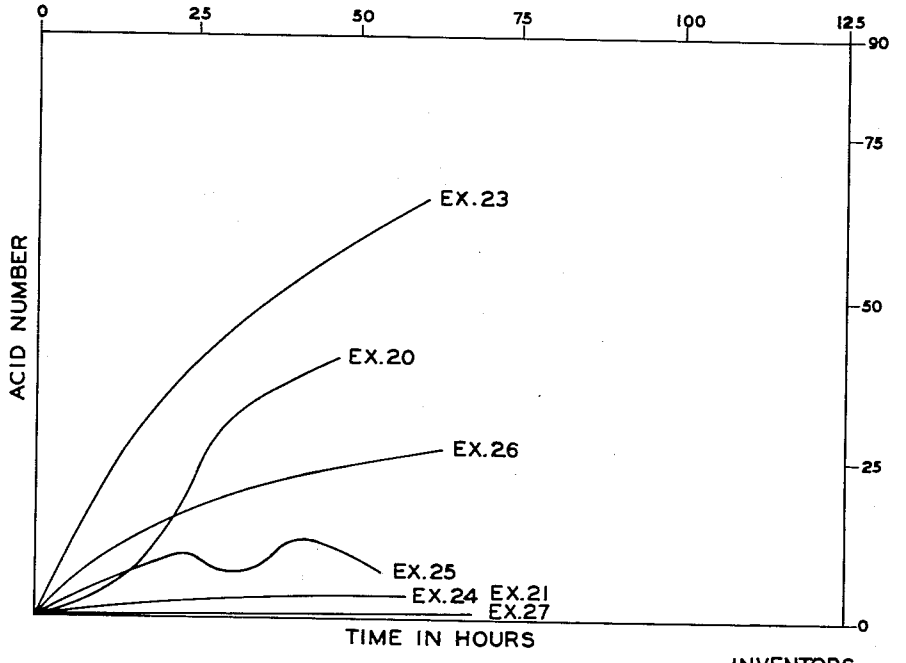


FIGURE 6

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United States Patent Office 2,987,536 Patented June 6, 1961

2,987,536

OXIDATION PROCESS

Hugh B. Skees, Afton, and Franklin E. Mange, University City, Mo., assignors to Petrolite Corporation, Wilmington, Del., a corporation of Delaware

Filed June 13, 1958, Ser. No. 741,766
16 Claims. (Cl. 260—451)

This invention relates to the oxidation of oxidation resistant hydrocarbons in the presence of a peroxide which is relatively heat stable and non-volatile under oxidation conditions. More particularly, this invention relates to the oxidation of said hydrocarbons with an oxygen-containing gas in the presence of an aralkyl-peroxide. In its most advantageous aspect, this invention relates to the oxidation of nondistillable hydrocarbons which are normally oxidation resistant, for example, sour microcrystalline waxes, hydrocarbons obtained from deoiling petrolatum in the preparation of residual microcrystalline wax, etc., by a process which comprises oxidizing said hydrocarbons with an oxygen-containing gas in the presence of a catalyst system comprising (1) an aralkyl peroxide such as dicumyl peroxide, (2) a basic material such as a non-amino base, and (3) a conventional oxidation catalyst, for example the oil-soluble salts of manganese, cobalt, chromium, vanadium, lead, zinc, etc.

A variety of hydrocarbon waxes and comparable compounds principally hydrocarbon in ntaure have been subjected to oxidation by various methods and particularly by the use of air, ozone, or oxygen in the presence of a conventional oxidation catalyst, for example a hydrocarbon-soluble organic salt, such as manganese or cobalt naphthenate.

These waxes and oher non-distillable hydrocarbons employed in oxidation may be obtained by various procedures. For instance, they may be obtained in processes involving the production of lubricating oil, such as from various lube oil stocks and petrolatums, or in processes conducted primarily for the recovery of wax; or they may be obtained from sediment in crude oil itself, i.e., commonly referred to as "tank bottoms."

The recovery and production of microcrystalline wax is well known and has been described in the literature. See, for example, U.S. Patent No. 2,443,840, dated June 22, 1948, to Stossel and in an article on "Microcrystalline Waxes, Their Manufacture, Properties and Uses in the Paper Industry" by Bruce H. Clary in "Industry and Paper World," February 1, 1956, page 19.

Recovery of tank bottom waxes is conducted principally in the mid-western oil fields, in Kansas, Oklahoma, Louisiana, and Texas as well as elsewhere to a lesser degree. The difference in tank bottom waxes can be illustrated by reference to those found in the State of Texas. The composition of tank bottom waxes has been approximately determined. In each instance the tank bottom wax is a mixture principally of hydrocarbon material containing perhaps a trace of some other element in chemical combination, not infrequently oxygen, and sometimes nitrogen and sulfur. Although there usually is only a trace of elements other than carbon and hydrogen, yet such trace in combination with a molecule having 35 to 100 carbon atoms may actually have significance which is somewhat obscure and subtle.

Although the tank bottom waxes are largely paraffinic in nature, one cannot rule out the possibility that a molecule having 35 to 100 carbon atoms may or may not have some other structure such as an aryl structure or more likely an alicyclic structure.

Even in light of what has been said previously, there is no explanation for a fact that has been recognized for years, namely, that microcrystalline waxes, even if one limits oneself to those found in Texas, fall into two

classes; one class consists of oxidation susceptible microcrystalline waxes which can be oxidized readily using a conventional catalyst and using a well known conventional procedure such as the kind described in the article entitled "Oxidation of Paraffins" by Dr. Ernest Stossel, which appeared in the Oil and Gas Journal, issues of July 21, August 18, and September 1, 1945. The other class of microcrystalline waxes appears to be identical in most respects but for some reason these are not oxidation susceptible waxes and for some purposes perhaps they are even more valuable.

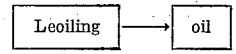
Purely for purpose of illustration, immediately following and identified as Table I, is a table showing oxidation of the West Texas microcrystalline wax (non-oxidation susceptible), the oxidation of an East Texas microcrystalline wax (oxidation susceptible), and the oxidation of an aluminum chloride treated West Texas microcrystalline wax, all three waxes being oxidized under the same conditions, namely with the conventional cobalt naphthenate catalyst by the method described by Dr. Ernest Stossel above.

TABLE I

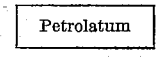
	Duration of Oxidation, Hours	Temperature, ° F.	Acid No. of Product
East Texas Wax	16	330	31.6
West Texas Wax	24	330	1.9
West Texas Wax (aluminum chloride treated)	8	330	26.1

Thus, one can select two different microcrystalline waxes, both obtained from tank bottoms and both possibly obtained from the same state, for instance, from various Texas oil fields which are characterized by substantially the same physical properties by conventional measurements, but from the standpoint of oxidation susceptibility by means of gaseous oxidation it is found that one class is non-susceptible and the other one is susceptible. The non-susceptible type of wax when reacted prior to oxidation with aluminum chloride or other halides, such as hydrochloric acid, or certain Friedel-Crafts catalysts, becomes oxidation susceptible. The above aluminum chloride treatment was accomplished by heating for approximately 7 hours at 100° C. The amount of aluminum chloride used was 10%. Such treatment has been described in the patent literature for example, in U.S. Patent No. 2,471,102. However, the use of aluminum chloride to render these waxes oxidation susceptible is a long, tedious and expensive process.

Another non-distillable, oxidation-resistant hydrocarbon is an oil separated in the deoiling of petrolatum stock used in the preparation of residual microcrystalline wax. This oil is described in the above Bruce Clary article and is separated by a procedure shown in FIGURE 1 of that article on page 19, under the Residual Micro Wax flow sheet under



which follows



This oil, which we shall refer to as "V-Oil" has a molecular weight of about 600, is relatively paraffinic, has a viscosity index of about 130, density of about 0.82 at 210° F. and a viscosity-gravity constant of about 0.79. Various correlative methods indicate that each molecule con-

tains an average of 6 naphthenic and 3 aromatic carbon atoms. It contains no materials which will complex with urea, indicating that it is highly branched. It has the following specifications:

Flash	400° F. min.
Gravity (API)	26/32
Color	dark
Visc. @ 210 (Saybolt)	80/120
Cold test	70/110
B.S. and W.	1% mx.

We have now discovered that non-distillable oxidation resistant hydrocarbons such as those described above can be most advantageously oxidized without the conventional $AlCl_3$ pretreatment by a process which comprises (A) oxidizing said hydrocarbons with an oxygen-containing gas in the presence of a catalyst system comprising (1) an aralkyl peroxide, such as dicumyl peroxide, (2) a basic material, such as a non-amino base, and (3) a conventional oxidation catalyst, for example the oil-soluble salts of manganese, cobalt, zinc, iron, chromium, vanadium, lead, etc. In addition, these oxidation resistant hydrocarbons can be oxidized, although not as effectively as with the above treatment, by the following catalyst systems, (B) a base, most preferably a non-amino base, and the conventional oxidation catalyst (C) an aralkyl peroxide and the conventional catalyst, (D) an aralkyl peroxide and a base and (E) an aralkyl peroxide. In fact, the presence of the aralkyl peroxide enhances the effectiveness of any particular catalyst system we have tried. However, the most effective results are obtained with (A).

The oxidation process

Except for the presence of the unique catalyst systems of this invention, the oxidation is carried out in the manner heretofore employed in oxidizing wax-type hydrocarbons. In general, these processes comprise treating the hydrocarbon stock with an oxygene-containing gas such as air, ozone, oxygen, etc., at a temperature above the melting point of hydrocarbon stock, but below its decomposition temperature, such as the range of 100° to 200° C., for example, 110° to 160° C. but preferably 115° to 130° C. The oxidation is continued for a sufficient length of time to give the desired acid number which time might vary from 5 to 50 or more hours, for example, 10 to 30 hours, but preferably 15 to 20 hours. Of course, it will be realized that there is an inter-relation of temperature and time for each particular system. Other variations also tend to influence the oxidation. For example, the finest possible division of the oxygen-containing gas employed for the oxidation tends to increase the oxidation rate. Increasing the oxygen pressure also accelerates the rate of oxidation. The rate of air addition can vary widely, such as from 0.1 to 20 ml./g/min., for example, from 0.5 to 5.0, but preferably from 1.0 to 3. Of course, other factors will influence these rates. For example, with pure oxygen or oxygen enriched air, lower rates can be used. On the other hand, higher rates would be required if the oxidizing gas is not finely dispersed.

Examples of the usual oxidation procedures are described in U.S. Patent No. 2,249,708, dated July 15, 1941, to Hicks-Bruun; U.S. Patent No. 2,486,454, dated November 1, 1949, to Zellner; U.S. Patent No. 2,573,422, dated October 30, 1951, to Fish; and U.S. Patent No. 2,674,613, dated April 6, 1954, to Nelson. Also, the three-part article entitled "Oxidation of Paraffins" by Ernest Stossel in The Oil and Gas Journal, vol. 44, No. 11, pp. 130–9; No. 15, pp. 145–51; No. 17, pp. 69–77 (1945) should be especially noted and also the 121 references in this article.

The oxygenation products of the invention can vary widely depending on the use for which they are intended. For convenience, the main criteria we employ for determining the extent of oxidation are acid numbers. In general, we prefer that the oxidized product have an acid number of at least 10, for example, 10 to 100 or more, but preferably 25 to 70, and a combined oxygen content of at least 2%. However, the optimum amount of oxidation can be varied according to the use intended. For example, for use as emulsifiable wax, the product should have an acid number of at least 10–15, but preferably about 20 to 40.

The oxidation can be carried out in a batch or continuous operation. In the case of the continuous operation care should be taken that, if possible little, if any, admixing of the fresh wax stock occurs with the already oxidized product. That is the product is introduced and passed through the oxidation apparatus in a uniform manner. This can be achieved by the following provision:

(1) Oxidation in several reaction vessels, placed one above another, or in series; (2) oxidation in sub-divided reaction vessels, or expediently in pipes; (3) oxidation in a reaction coil, arranged in a spiral in which the wax is introduced at the top and the reaction product leaves at the bottom.

The basic material

Any basically reacting agent capable of enhancing the oxidation of the difficultly oxidizable material can be employed. In general, the basic material is a non-amino base.

They can include the use of alkali metal and alkaline earth metal hydroxides, oxides, alkoxides, and also salts of these metals with weak, inorganic and organic acids, for example those derived from group IA and IIA of the periodic table.

As examples of the alkali metal and alkaline earth metal hydroxides, there may be mentioned sodium hydroxide, potassium hydroxide, lithium hydroxide, calcium hydroxide, barium hydroxide, strontium hydroxide, and magnesium hydroxide. The alkoxides are represented by sodium n-butoxide, and the corresponding potassium, lithium, calcium, strontium, barium and magnesium alcoholates. Exemplary of the alkali metal salts of weak inorganic acids are sodium tetraborate, tri-sodium phosphate, and potassium carbonate. Examples of alkali metal salts of weak organic acids are those alkali metal salts of acids which form soaps, such as the higher fatty acids, for example, stearic, oleic, palmitic, lauric, linoleic, ricinoleic, the commercially available mixtures obtained by the hydrolysis or saponification of commercial oils or fats; the resin acids or commercial rosins and their modifications, such as dihydroabietc acid, tetrahydroabietic acid, dehydroabietic acid, hydroxytetrahydroabietic acid, hydrogenated rosin, disproportionated or dehydrogenated rosin, and polymerized rosin; and the naphthenic acids.

Basically reacting agents found to be of particular value in the process include the alkaline earth metals, calcium, magnesium, strontium and barium and the oxides, hydroxides and carbonates of these metals; the basically reacting oxides, hydroxides, and carbonates of the metals of the iron group which metals include iron, cobalt and nickel; the basically reacting oxides, hydroxides and carbonates of the metals of the right-hand column of group II of the periodic table which are not classifiable as alkaline earth metals, which metals include beryllium, zinc, cadmium and mercury; and the oxides, hydroxides, carbonates and bicarbonates of the alkali metals sodium, potassium and lithium.

In employing these basically reacting agents, we may use them in finely divided form, such as in the form of a powder, or those which are water-soluble may be used in the form of a dilute aqueous solution. The powdered compounds may be made into a slurry or otherwise suspended in the hydrocarbon fraction being oxidized and the suspension maintained by means of mechanical agita-

tion and/or by means of air, or other oxygen-containing gas agitation during the oxidation process. In a batch operation sufficient of the basically reacting agent may be added at the start of the oxidation or a portion of the required agent may be added and sufficient additional quantities added during the progress of the oxidation. In a continuous operation, it is generally preferable to mix the total quantity of basically reacting agent with the hydrocarbon feed to the oxidizer.

When employing water-soluble basically reacting agents, an aqueous solution of the agent may be injected into the oxidation unit with the feed, with the air or oxidizing gas or at any other convenient point. Thus, a saturated aqueous solution of calcium hydroxide containing an excess of calcium hydroxide may be injected into the oxidation vessel in sufficient quantities. Aqueous solutions of alkali metal carbonates, bicarbonates or hydroxides may be similarly employed.

In using the alkaline earth metals themselves, it is convenient to use metal turnings or shavings, supporting them on trays or racks within the oxidation vessel. As a modification of the above processes, metals and other agents described which are not appreciably water-soluble may be employed in the form of shavings of granules of any convenient size in a secondary vessel outside of the oxidation vessel and the neutralization of acids effected by continuously pumping the hydrocarbon being oxidized from the oxidation vessel to the secondary vessel where it is contacted by the basically reacting agent and then returned to the oxidizer.

The amount of basic material employed in the catalyst can vary from 0.1 to 3% or higher, for example, 0.2 to 1.5%, but preferably 0.25 to 0.75% based on weight of hydrocarbon. Of course, the weight might vary somewhat according to the molecular weight of the base relative to its effective basicity.

The conventional oxidation catalyst

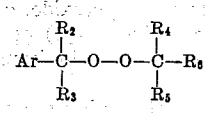
The term "conventional oxidation catalyst" refers to those metallic compounds heretofore conventionally employed by the art in the oxidation of wax type hydrocarbons, for example, compounds of manganese, cobalt, lead, iron, nickel, copper, vanadium, chromium, mercury, zinc, etc. Since greater activity is achieved by using a soluble compound these are preferred. Metal salts of organic acids are particularly useful in this invention. Exemplary of such salts are manganese-butyl phthalate, manganese linoleate, manganesse naphthenate, a mixture of manganese and lead acetates, cobalt linoleate, cobalt naphthenate, mixed lead-cobalt naphthenate, the metal resinates such as manganese, cobalt, zinc, etc. resinates derived from any rosin acid such as abietic, pimaric, dehydroabietic, dihydroabietic, tetrahydroabietic acid, cobalt acetate, cobalt oleate, cobalt stearate, and corresponding organic acid salts of the other metals can also be employed. Other examples of conventional oxidation catalysts can be found in the patents describing the oxidation of hydrocarbons disclosed in the section of this patent relating to the oxidation process. In general, these catalysts are heavy metal compounds.

The conventional oxidation catalyst can vary from .1 to 3% or higher, for example, 0.2 to 1.0%, but preferably 0.3 to 0.7%, based on weight of hydrocarbon. These figures are based on cobalt naphthenate containing 6% cobalt, the preferred catalyst. For other catalysts, these figures will vary somewhat according to the molecular weight of the catalyst relative to the percent of metal present therein.

The peroxide

Although many peroxides aid somewhat in the present oxidation system, their effect is generally dissipated before a suitable acid number is obtained. For example, when dibenzoyl peroxide is employed, its presence is effective in the catalyst system for only a short period of time after

which time its effect is diminished. Ditertiary butyl peroxide is also relatively ineffective. In contrast, where a peroxide having the properties of an aralkyl peroxide is employed, one obtains the superior results of this invention. These peroxides are represented by the structural formula



where Ar is an aryl group, for example, phenyl, naphthyl, anthryl, phenanthyl, etc. The aryl group may contain alkyl substituents as in the case of isopropylphenyl, butylphenyl, isobutylphenyl, t-butylphenyl, pentamethyl, ethylphenyl, dimethylphenyl, methylethylphenyl, etc. and the corresponding alkyl derivatives of the other aryl groups mentioned above. Thus, the term aryl includes alkaryl groups. The aryl group may also contain other groups that do not interfere with the usual effect of the peroxide on the instant catalyst system. R_2, R_3, R_4, and R_5, which may be the same or different, are hydrogens or alkyl groups of less than 4 carbons. R_6 is hydrogen, an alkyl of less than 4 carbons, or Ar, which has the same meaning as Ar of the present formula. Where R_6 is Ar it need not be the same as the other Ar group.

In other words these peroxides contain one or two aryl groups. They may be symmetrical or unsymmetrical and mixtures of them may be employed.

In general, the peroxides of this invention are characterized by containing at least 10 carbon atoms and usually not more than about 40 carbon atoms. Specific peroxides preferred in the invention are methyl (α,α-dimethylbenzyl) peroxide, tertiary butyl (α,α-dimethylbenzyl) peroxide, methyl (α,α-dimethyl-p-isopropylbenzyl) peroxide, and methyl (α-α-dimethyl-p-methylbenzyl) peroxide, bis (α,α-dimethylbenzyl) peroxide, bis (α,α-dimethyl-p-methylbenzyl) peroxide, and bis (α,α-dimethyl-p-isopropyl-benzyl) peroxide. The peroxide most advantageously employed is dicumyl peroxide [bis(α,α-dimethyl benzyl) peroxide].

The class of di(aralkyl) peroxides of this invention include the following symmetrical or bis(aralkyl) peroxides: dibenzyl peroxide, bis (α-methylbenzyl) peroxide, bis(α-ethylbenzyl) peroxide, bis(α-propylbenzyl) peroxide, bis(α-isopropylbenzyl) peroxide, bis(α,α-dimethylbenzyl) peroxide, bis(α-methyl-α-ethylbenzyl) peroxide, bis(α,α-diethylbenzyl) peroxide, bis(α,α-dipropylbenzyl) peroxide, bis(α,α-diisopropylbenzyl) peroxide, bis (α,α-diisopropylnaphthylmethyl) peroxide, bis(α,α-dimethylnaphthylmethyl) peroxide, bis(α,α-dimethyl-p-methylbenzyl) peroxide, bis(α-methyl-α-ethyl-p-methylbenzyl) peroxide, bis(α,α-diethyl-p-methylbenzyl) peroxide, bis-(α,α-diisopropyl-p-methylbenzyl) peroxide, bis(α,α-dimethyl-p-ethylbenzyl) peroxide, bis(α-methyl-α-ethyl-p-ethylbenzyl) peroxide, bis(α,α-diethyl-p-ethylbenzyl) peroxide, bis(α,α-diisopropyl-p-ethylbenzyl) peroxide, bis(α,α-dimethyl-p-isopropylbenzyl) peroxide, bis(α-methyl-α-ethyl-p-isopropylbenzyl)peroxide, bis(α,α-diethyl-p-isopropylbenzyl) peroxide, bis (α,α-diisopropyl-p-isopropyl-benzyl) peroxide, bis(α,α-dimethyl-p-t-butylbenzyl) peroxide, bis(α-methyl-α-ethyl-p-t-butylbenzyl) peroxide, bis(α,α-diethyl-p-t-butylbenzyl) peroxide, bis (α,α-diisopropyl-p-t-butylbenzyl) peroxide, bis(α,α-dimethyl-p-pentamethylethylbenzyl) peroxide, bis (α-methyl-α-ethyl-p-pentamethylethylbenzyl) peroxide, bis (α,α-diethyl-p-pentamethylethylbenzyl) peroxide and bis (α,α-diisopropyl-p-pentamethylethylbenzyl) peroxide.

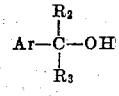
Unsymmetrical diaryl peroxides of this invention containing two aryl groups include the following compounds. benzyl(α-methylbenzyl) peroxide, benzyl(α-methyl-p-methylbenzyl) peroxide, benzyl(α-methyl-p-isopropylbenzyl) peroxide, benzyl(α,α-dimethylbenzyl) peroxide benzyl-(α,α-dimethyl-p-methylbenzyl) peroxide, benzyl

(α,α-dimethyl-p-isopropylbenzyl) peroxide, α-methylbenzyl(α,α-dimethylbenzyl) peroxide, α-methylbenzyl(α,α-dimethyl-p-methylbenzyl) peroxide, α-methylbenzyl(α,α-dimethyl-p-methylbenzyl) peroxide, α-methylbenzyl(α,α-diemthyl-p-isopropylbenzyl) peroxide, -isopropylbenzyl (α,α-diisopropylbenzyl) peroxide, α,α-dimethylbenzyl(α,α-dimethyl-p-methylbenzyl) peroxide, α,α-diisopropylbenzyl-(α,αdiisopropyl-p-methylbenzyl) peroxide, and α,α-diisopropylbenzyl (α,α-diisopropyl-p-isopropylbenzyl) peroxide.

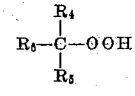
The peroxides of the invention are nonvoltatile peroxides, having a vapor pressure sufficiently low at oxidation temperatures to prevent substantial loss of the peroxide during oxidation. The nonvolatile peroxides of the invention are thus distinguished from volatile peroxides such as di(tertiary butyl) peroxide. In general, the peroxides of the invention have boiling points greater than about 150° C.

The peroxides of the invention decompose at a moderate rate under oxidation conditions to form free radicals. Thus, for example, methyl (α,α-dimethylbenzyl) peroxide decomposes to form a methoxy free radical and an α,α-dimethylbenzyloxy free radical. The decomposition of the peroxides is almost entirely dependent upon temperature.

The peroxides of the invention can be prepared by methods known to the art. A particularly convenient method involves condensation of the corresponding alcohols of the general formula



and hydroperoxides having the general formula



wherein Ar, R_2, R_3, R_4, R_5 and R_6 are the same as in the general formula given hereinabove. The amount of alcohol utilized should be at least the theoretical calculated amount to combine with all of the hydroperoxide and preferably slightly in excess of this amount. The condensation of the hydroperoxide with the alcohol is carried out in the presence of a catalytic amount up to about 0.5% of an acid-acting condensation catalyst based on the weight of the alcohol, and the temperature used is preferably between 50°–120° C. p-toluene sulfonic acid can be utilized as the acid-acting condensation catalyst. The hydroperoxides and alcohols mentioned above may be prepared in accordance with processes well known to the art.

The peroxides of the invention in which R_4, R_5 and R_6 are all hydrogen can be produced conveniently by contacting aralkyl hydroperoxides with dimethyl sulfate in an aqueous alkaline medium. For example, methyl (α,α-dimethylbenzyl) peroxide can be produced by dispersing cumene hydroperoxide with rapid stirring in an aqueous solution of sodium hydroxide while gradually adding a stoichiometric amount of dimethyl sulfate and maintaining the temperature at about 25–30° C. After all the dimethyl sulfate is added and the reaction is complete, the methyl (α,α-dimethylbenzyl) peroxide can be taken up in petroleum ether and washed free of cumene hydroperoxide with 10% aqueous sodium hydroxide. The desired peroxide can then be recovered in a purity of about 90% by distilling off petroleum ether.

The amount of peroxide utilized in the catalyst system of our invention can vary within wide limits, depending upon the particular hydrocarbon oxidized and its oxidation resistance. Of course, high concentrations can be employed if desired, but the economics of the process require the most efficient use of the peroxide. Thus, a concentration of 0.2 to 4% or higher of the peroxide based on weight of the hydrocarbons, for example, 0.3 to 2.0%, but preferably 0.5 to 1.0% can be employed.

The following examples are presented to illustrate our invention. The percentages of catalyst employed are by weight percentages based on the weight of the hydrocarbon stock.

In general, the hydrocarbon stock is oxidized at 120° C. by blowing air at the rate of 2–3 ml./g./min. through a sintered glass disperser into the molten hydrocarbon stock under the conditions indicated in the following table. The following non-oxidation susceptible hydrocarbon stocks are oxidized: (1) Ultraflex Amber—a plastic microcrystalline wax derived from petrolatum stock by a centrifuge process and then bleached to a color of 2NPA by percolation through activated clay. It has a melting point of 140–145° F. (ASTM test method D127–30) and a penetration of 25–30 at 77° F. (ASTM test method D5–25); (2) Bleached West Texas Microcrystalline Wax—a hard microcrystalline wax obtained from tank bottoms from West Texas crude oil, which is a sour crude. Bleached West Texas crude is derived from this sour crude and bleached by percolation through activated clay to a color of about 1.5 NPA. It still has the characteristic sour crude odor. It has a melting point of 190–200° F. and a penetration (Pen 100/5@ 77° F.) of 4–5 at 77° F.; and (3) Black V-Oil, which has been described above. Bleached V-Oil has substantially the same properties except that it is lighter in color (1 to 2 NPA). It is bleached with clay. The black V-Oil is more oxidation resistant than the bleached V-Oil.

TABLE II

ULTRAFLEX AMBER MICROCRYSTALLINE WAX

Ex.	Peroxide	Percent Peroxide	Base	Percent Base	Conventional Oxidation Catalyst	Acid Number						
						5 hrs.	10 hrs.	20 hrs.	30 hrs.	40 hrs.	60 hrs.	80 hrs.
1	None		None		None	(1)	(1)	(1)	(1)	(1)	(1)	(1)
2	do		MgO	1.0	do	0	0.3	0.2	0.7	0.3	0.2	1.8
3	Dicumyl Peroxide	1.0	None		do	1.2	2.4	3.5	5.0	7.6	16.0	36.8
4	do	1.0	MgO	1.0	do	0.8	1.9	6.8	20.0	53.0	68.0	
5	do	2.0	MgO	1.0	do	1.8	5.0	15.3	27.8	46.5		
6	Dibenzoyl	2.0	MgO	1.0	do	4.3	6.3	8.8	15.0	23.5		
7	Dicumyl Peroxide	1.0	MgO	0.25	do	0.9	2.5	9.4	17.6	27.5		
8	do	1.0	MgO	0.5	do	0.6	1.7	7.0	14.0	22.5		
9	do	1.0	MgO	0.1	do	0.2	1.2	5.0	9.5	13.8	16.2	

[1] Substantially no oxidation during 80 hours.

TABLE III

WEST TEXAS MICRO-CRYSTALLINE WAX, BLEACHED

Ex.	Peroxide	Percent Peroxide	Base	Percent Base	Conventional Oxidation Catalyst	Percent Conventional Oxidation Catalyst	5 hrs.	10 hrs.	20 hrs.	30 hrs.	40 hrs.	60 hrs.	80 hrs.
10	Dicumyl Peroxide	2.0	MgO	1.0	None		1.2	2.3	6.6	15.6	20.3		
11	Dibenzoyl	2.0	MgO	1.0	do			6.0	5.4	4.8	4.0	3.3	
12	None		None		Cobalt Naphthenate	0.5	0.4	0.6	1.2	2.1	2.5	4.1	
13	do		MgO	1.0	do	0.5	0.2	0.6	2.0	20.5	56.0		
14	Dicumyl Peroxide	1.0	None		do	0.5	0.8	1.4	2.4	2.6	2.7	3.2	
15	do	1.0	MgO	1.0	None		0.2	0.3	1.4	3.1	4.6	7.8	
16	do	1.0	MgO	1.0	Cobalt Naphthenate	0.5	3.6	14.1	37.5	57.7	81.0		
17	do	1.0	MgO	1.0	do	0.5	0.1	9.3	39.5	60.2	76.5		
18	do	1.0	CH_3ONa	0.5	do	0.5	2.5	15.5	40.0	56.5	66.7	74.5	
19	None				None		[1]	[1]	[1]	[1]	[1]	[1]	[1]

[1] Substantially no oxidation during 60 hours.

TABLE IV

BLEACHED V-OIL

Ex.	Percent Dicumyl	Percent Base	Percent Cobalt Naphthenate	5 hrs.	10 hrs.	20 hrs.	30 hrs.	40 hrs.	50 hrs.	60 hrs.
20	2	1 MgO	None	1.5	4.6	14.5	30			
21	0	0	0	[1]	[1]	[1]	[1]	[1]	[1]	[1]
22	0	0	1.0	[1]	[1]	[1]	[1]	[1]	[1]	[1]
23	1	0.5 MgO	0.5	10	20	34	45	52	59	65

BLACK V-OIL

24	2	1 MgO	None	0.5	1.5	2.6	3.1	3.5	3.6	
25	2	0.5 CH_3ONa	0.5	1.5	3.1	9.2	7.5	12.1	9.3	
26	4	1 MgO	0.5	1.5	5.4	14.1	19.0	21.0	22.8	23
27	0	0	0	[1]	[1]	[1]	[1]	[1]	[1]	[1]
28	0	0	1.0	[1]	[1]	[1]	[1]	[1]	[1]	[1]

[1] Substantially no oxidation during 60 hours.

The data obtained in the above table is presented in the drawing in which FIGURE 1 through FIGURE 6 are graphs wherein acid number is plotted as a function of time in hours. The number identifying each curve refers to the examples in the above table.

From the above examples and graphs, it is evident that:

(1) The hydrocarbon stocks are substantially non-oxidation susceptible when oxidized (*a*) without any catalyst, (*b*) with only the base as a catalyst, (*c*) with only the conventional oxidation catalyst.

(2) The hydrocarbon stocks are more readily oxidized by a catalyst system containing both the conventional oxidation catalyst and the base than by either one alone.

(3) The hydrocarbon stocks are more readily oxidized with or without any other catalyst, provided the peroxides of this invention are employed. In other words, these peroxides enhance the effect of any particular oxidation system.

(4) The hydrocarbon stocks are most readily oxidized with a catalyst system containing the peroxides of this invention, a base, and the conventional oxidation catalyst.

The products of this invention can be employed in many applications, for example—the oxidized microcrystalline wax can be employed in wax emulsions, polishes, which can be spread on surfaces such as linoleum, wood floors, furniture, automobiles, etc., to give a finish which dries to a high gloss. These oxidized hydrocarbons also find use as additives for lubricating greases or as additive in various hydrocarbon coating for metals which, in addition to enhancing the physical properties, they also have a tendency to inhibit corrosion. In addition, these oxidized hydrocarbons can be employed as the acid moiety of salts of various amines, for example, the "Duomeens," $RNH(CH_2)_3NH_2$, where R is a hydrocarbon radical, for use as corrosion inhibitors, in oil wells, slushing oils, etc.

We claim:

1. A process of oxidizing normally non-distillable oxidation resistant petroleum hydrocarbons which comprises oxidizing said hydrocarbons with an oxygen containing gas at a temperature above their melting point but below their decomposition temperature in the presence of at least 0.2% of an aralkyl peroxide having at least 10 carbon atoms and boiling above 150° C. which is relatively heat stable and non-volatile under the oxidizing conditions.

2. The process of claim 1 where the peroxide is dicumyl peroxide.

3. A process of oxidizing normally non-distillable oxidation resistant petroleum hydrocarbons which comprises oxidizing said hydrocarbons at a temperature above their melting point but below their decomposition temperature with an oxygen containing gas in the presence of at least 0.1% of a basic material and at least 0.2% of an aralkyl peroxide having at least 10 carbon atoms and boiling above 150° C. which is relatively heat stable and non-volatile under the oxidizing conditions.

4. The process of claim 3 where the basic material is a non-amino base.

5. The process of claim 4 where the peroxide is dicumyl peroxide.

6. A process of oxidizing normally non-distillable petroleum hydrocarbons which are normally oxidation resistant which comprises oxidizing said hydrocarbons at a temperature above their melting point but below their decomposition temperature with an oxygen-containing gas in the presence of (1) at least 0.2% of an aralkyl peroxide having at least 10 carbon atoms and boiling above 150° C. which is relatively heat stable and non-volatile under the oxidizing conditions (2) at least 0.1% of a basic material and (3) at least 0.006% based on metal content of an oxidation catalyst.

7. The process of claim 6 where the basic material is a non-amino base.

8. The process of claim 7 where the peroxide is dicumyl peroxide.

9. The process of oxidizing normally non-distillable oxidation resistant petroleum hydrocarbons which comprises oxidizing said hydrocarbons with an oxygen-containing gas at a temperature above their melting point but below their decomposition temperature with an oxygen containing gas in the presence of (1) at least 0.2% dicumyl peroxide (2) at least 0.1% of a non-amino base selected from the group consisting of alkali metal and alkaline earth salts and (3) at least 0.006%, based on metal content of an oxidation catalyst containing a heavy metal.

10. The process of claim 9 wherein the oxidation catalyst is selected from the group consisting of cobalt and manganese compounds.

11. The process of claim 9 where the oxidation resistant hydrocarbons are a microcrystalline wax.

12. The process of claim 9 where the oxidation resistant hydrocarbons are an oil extracted from petrolatum stock.

13. The process of claim 11 where the process is carried out at 110–160° C. in the presence of a member selected from the group consisting of a group IA base and a group IIA base and an oil soluble heavy metal compound.

14. The process of claim 13 where the process is carried out in the presence of MgO and cobalt naphthenate.

15. The process of claim 12 where the process is carried out at 110–160° C. in the presence of a member selected from the group consisting of a group IA base and a group IIA base and an oil soluble heavy metal compound.

16. The process of claim 15 where the process is carried out in the presence of MgO and cobalt naphthenate.

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