

UNITED STATES PATENT OFFICE

2,588,902

PEROXIDE TREATMENT OF FATTY OILS

Leonard P. Wiebe, Long Beach, Calif., assignor to
 Shell Development Company, Emeryville, Calif.,
 a corporation of Delaware

No Drawing. Application September 26, 1950,
 Serial No. 186,926

8 Claims. (Cl. 260—405.6)

1

This invention relates to a method for improving the drying properties of unsaturated fatty oils of marine, vegetable and animal origin, as well as to the new and improved products obtainable thereby, which products are particularly adapted for use in the paint, lacquer, varnish and linoleum industries. More particularly, the invention pertains to treatment of unsaturated fatty oils with a peroxide containing a tertiary-alkyl peroxy radical whereby a product having excellent drying properties is obtained.

Drying oils such as linseed oil have long been used in the manufacture of paints, varnishes, inks, etc. Such oils as linseed oil have been considered quite satisfactory for such purposes although considerable room for improvement has been recognized with regards to ability of films of the oil to dry hard. Other oils such as fish oil and soy bean oil have been quite unsatisfactory because the oil will not dry to a hard film, but instead the film tends to remain sticky or tacky.

It has now been discovered that new products having excellent drying properties are obtained by heating a fatty oil having an iodine value above 120 at about 100° C. to 250° C. in the presence of a peroxide containing a tertiary-alkyl peroxy radical. Not only does the treatment convert such oils as fish oil and soy bean oil into products which dry to hard films free of tack or stickiness, but also, the treatment enables oils like linseed oil to be converted to products which dry to hard films.

The action of the peroxide containing a tertiary-alkyl peroxy radical in the process of the invention appears to be unique. Thus, while it has previously been proposed to heat fatty oils with various peroxides, particularly benzoyl peroxide, for the purpose of bleaching the oil, treatment with such peroxides does not give products having the outstanding drying properties of the

oils of the present invention. The unique character of the action of the peroxides containing a tertiary-alkyl peroxy radical will be evident from the comparative results following.

Alkali-refined winterized sardine oil having an iodine value of 198 grams iodine per 100 grams of oil (determined by the Woburn method described by von Mikusch and Frazier, Ind. Eng. Chem., Anal. Ed., vol. 13, pages 782-9 (1941)) was employed for the tests in which the action of di-tertiary-butyl peroxide was compared with that of benzoyl peroxide and cumene hydroperoxide (2-phenyl-2-hydroperoxypropane). The sardine oil had been winterized to stand clear for 2 to 3 hours minimum at 32° F. The respective peroxides in the amount stated in Table I below were added to the oil in containers which were then immersed in a thermostatically controlled heating bath. In order to dissolve the benzoyl peroxide in the oil without preheating, it was added as a solution in twice its weight of benzene. A slow stream of carbon dioxide gas was passed through the oil mixtures to provide gentle agitation and exclude air. The oil mixtures containing the peroxides were upheated to 150° C. in one hour and maintained at this temperature for an additional 5½ hours. For comparison, an oil sample containing no peroxide was similarly heated. After cooling, cobalt octoate (cobalt 2-ethylhexoate) as drier in amount of 0.05% cobalt was added to the treated oils and to an untreated oil sample. The oils were then spread on glass plates with the aid of a 2 mil doctor blade and subjected to drying tests in a constant temperature room maintained at 77° F. and 50% relative humidity. The drying properties of the oils are given in Table I. The drying tests were conducted according to the procedures described by Henry A. Gardner in "Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors," 1939, pages 106-107.

TABLE I

Peroxide Added	Di-Tertiary-Butyl Peroxide	Benzoyl Peroxide	Cumene Hydro-Peroxide	None	None
Percentage Added	2.5	2.5	2.5	0	0
Heating Time in Hours:					
25° C. up to 150° C.					
at 150° C.	1	1	1	1	not heated.
Drying Properties:					
Set to touch	1.75 hrs.	2.75 hrs.	2.75 hrs.	2.75 hrs.	2.75 hrs.
Dust-free	1.5 hrs.	2.25 hrs.	2.25 hrs.	2.25 hrs.	2.25 hrs.
Tack-free	2.75 hrs.	less than 3 days	less than 3 days	less than 3 days	less than 3 days
Dry hard	less than 3 days	not in 10 days	not in 10 days	not in 10 days	not in 10 days

The tabulated results demonstrate the outstanding improvement achieved by heat-treating the oil with di-tertiary-butyl peroxide. Not only does the treated oil dry to a tack-free state in a few hours, but also, a film which is dried hard is also obtainable. On the other hand, treatment of the oil with benzoyl peroxide or cumene hydroperoxide gives a product having drying properties which are substantially the same as those of untreated oil or oil given heat treatment without peroxide.

The method of the invention is applicable to treatment of a wide variety of fatty oils. New products with marked improvement in drying properties are obtained by subjecting fatty oils having iodine values of at least 120 to the method. Among representative examples of drying oils improved by the method are such oils as sardine (pilchard), menhaden, whale, soy bean, hempseed, linseed, perilla, safflower, oiticica, walnut, tung and dehydrated castor. Although the oils may be used in raw condition, it is preferred that they first be subjected to one or more of the usual refining procedures such as so-called alkali-refining. Moreover, it is preferred that the fish oils be winterized in order that fractions containing stearin and the like be removed from the oil. It is preferred that the fish oil be winterized so as to stand clear for 2 to 3 hours at 32° F. If desired, mixtures of two or more different oils containing at least 5% of each may be treated.

In execution of the method, the mixture of oil and peroxide containing a tertiary-alkyl peroxide radical is heated at about 100° C. to 250° C. Depending somewhat upon the particular oil treated, the peroxide and its amount, and the temperature, the heating is continued for about 1 to 20 hours. Excellent results are obtained at temperatures of about 150° C. to 200° C. in 6 to 10 hours heating, and therefore, temperatures in this range are preferred with a temperature in the neighborhood of 175° C. being particularly suitable. The heating is discontinued prior to gellation of the oil since the treatment with the peroxide is not primarily a polymerization. In fact, the average molecular weight of the products having the new drying properties is usually not more than about 30% greater than that of the original oil although in some cases it may be desirable to continue the heating until the molecular weight has increased 50% or even doubled. Treated oil with molecular weight twice as great as that of the original oil is still far below the gellation point.

The heating may be conducted with the reaction mixture under ordinary atmospheric pressure, but when a temperature above the boiling point of the peroxide employed is used, it is desirable to utilize superatmospheric pressure sufficiently high that appreciable loss of the peroxide by boiling does not occur.

It appears that by far the best results and products are obtained by treatment with di-tertiary-butyl peroxide. If desired, however, any peroxide containing a tertiary-alkyl peroxy radical may be used such as, for example, di-tertiary-amyl peroxide, di-tertiary-octyl peroxide, monochloro-di-tertiary-butyl peroxide, symmetrical dichloro-di-tertiary-butyl peroxide, asymmetrical dichloro-di-tertiary-butyl peroxide, monobromo-di-tertiary-amyl peroxide, tertiary-butyl tertiary-amyl peroxide, isopropyl tertiary-butyl peroxide, ethyl tertiary-amyl peroxide, tertiary-butyl hydroperoxide, tertiary-hexyl hydroperoxide, monochloro-tertiary-butyl hydroperoxide, tertiary-butyl perbenzoate, tertiary-amyl peracetate, di-tertiary-

butyl perphthalate, 2,2-bis-(tertiary-butyl peroxy)propane, 2,2-bis-(tertiary-butyl peroxy)butane, 1-(tertiary-butyl peroxy)ethanol, and the like. In general, it is preferred to employ peroxides rather than hydroperoxides—i. e., compounds containing the tertiary-alkyl peroxy radical linked to another carbon atom. Single compounds are usually employed, but if desired, mixtures of two or more may be utilized—e. g., di-tertiary-butyl peroxide in admixture with tertiary-butyl hydroperoxide.

Various proportions of peroxide to oil are used in the invention. In general, about 0.5% to 10% of peroxide is added to the oil. Very good results are obtained with use of about an added 2% to 6% of peroxide. In executing the process, the total amount of the peroxide may be added to the oil and the mixture heated to effect the treatment. It has been found, however, that more efficient use of the treating agent is obtained by adding the peroxide portion-wise or continuously during the period of maintaining the oil at treatment temperature. In this procedure, the oil is usually heated to or about to the desired treatment temperature and the peroxide, as a concentrated solution of about 10% to 50% concentration in the same oil as treated, is added over a period of time while maintaining the temperature at the desired point. The heating may be continued for such time as desired after completion of the addition of the peroxide.

The action of the tertiary-alkyl peroxide on the oil whereby excellent drying properties are imparted thereto is not fully understood. Such peroxides are known to be polymerization catalysts for olefinically unsaturated compounds. However, the heat treatment with the peroxide does not cause substantial polymerization of the oil. Although the viscosity of the treated oil is considerably increased, the molecular weight is only slightly higher. This indicates that "bodying" is not a major factor in improvement of drying properties of the oil. Furthermore, there is only small decrease in iodine value of the treated oil. Examination of the ultraviolet absorption spectrum indicates that the peroxide treatment results in considerable conjugation as compared to the raw oil or oil heat-bodied in the absence of the peroxide. Moreover, the infra-red spectrum of the peroxide-treated oil and that of untreated oils demonstrates the presence of an increased amount of alpha-type olefinic groups



as well as transtype unsaturation. It therefore appears that the peroxide treatment causes considerable isomerization of new type on the oils.

Several specific embodiments of the invention are given in the following examples, but it is to be understood that the invention is not limited to details therein.

Example I

A mixture of 5% di-tertiary-butyl peroxide and 95% of alkali-refined winterized sardine oil was heated for 5 hours at 175° C. which caused the Gardner-Holdt viscosity of the oil to increase from A to O-P. This sardine oil as well as that described in the examples following had been winterized to stand clear for 2 to 3 hours minimum at 32° F.

For purposes of comparison and in order to have a heat-bodied product having approximately the same viscosity as the peroxide-treated oil, a sample of raw oil was heated up to 300° C. in 80 minutes and maintained at this temperature for

TABLE IV

	Untreated Oil	Treated Oil
Viscosity, Gardner-Holdt	A	G-H.
Refractive index, n_D^{20}	1.4750	1.4793
Drying time, hours:		
Set to touch	6.25	4.25
Dust free	8	6
Tack free		6.5
Hard dry		7.75

TABLE II

Oil	Peroxide-Treated	Untreated	Heat-Bodied
Viscosity, Gardner-Holdt	O-P.	A	N.
Iodine value, Wijs	153	183	230
Molecular weight	925	897	1210
Refractive index, n_D^{20}	1.4856	1.4818	1.4861
Drying Time:			
Set to touch	1 hour	4 hours	5.5 hours
Dust free	1.5 hours	5.5 hours	more than 7 hours
Tack free	2 hours	6.5 hours	not in 50 hours
Hard	4 hours	not in 50 hours	
Cotton free	6.5 hours		

Example II

A series of treatments at different temperatures were effected on alkali-refined winterized sardine oil while continuously adding di-tertiary-butyl peroxide. The oil was placed in a glass reaction vessel equipped with a stirrer and dropping funnel. The vessel was immersed in a thermostatically controlled bath and a very slow stream of nitrogen was bubbled through the charge. The oil was heated to treatment temperature in about 50 minutes and then the peroxide as a solution of 15 parts by weight in 100 parts of oil was added dropwise from the dropping funnel. After all the peroxide had been added, heating was continued for about 45 minutes additional time. Table III gives details of the treatment along with results of drying tests of films containing 0.05% cobalt as cobalt octoate prepared using a 2 mil doctor blade and dried at 77° F. and 50% relative humidity.

TABLE III

Per cent Peroxide	None	None	5.5	5.6	5.6	3.2
Temperature, ° C.	150	150	175	200	225	
Time, hours	5.5	10	6.5	6.5	3.5	
Refractive Index n_D^{20}	1.4827	1.4824	1.4862	1.4880	1.4895	1.4859
Molecular Weight	897	870	1205	1250	1385	970
Viscosity, Gardner-Holdt	A-A1	A-A1	D	G-H	O-P	B-C
Iodine value, Woburn	193	203	189	181	173	185
Drying time, hours:						
Set to touch	2.75	2.75	1.5	1	1	2
Dust free	3	2.25	1.75	1.25	1.25	2.25
Tack free	not in 240	less than 72	3.5	2.25	3	
Hard		not in 10 days	4.5	2.75	3.75	

Example III

Alkali-refined winterized sardine oil was treated as described in Example II at 175° C. for 6 hours with 5.6% of tertiary-butyl hydroperoxide. The treated oil had a Gardner-Holdt viscosity of G+ and a refractive index (n_D^{20}) of 1.4871. Drying tests conducted as described above gave the following results: Set to touch 1.75 hours, dust free 2 hours, tack free 3.5 hours, and hard dry 5.25 hours.

Example IV

Alkali-refined soy bean oil was treated as described in Example II at 175° C. for 6 hours with 5.6% di-tertiary-butyl peroxide. The results including drying tests effected as described hereinbefore follow.

10

25

30

40

35

45

50

55

60

65

60

70

70

75

TABLE V

	Heat-Bodied Oil	Peroxide-Treated Oil
Refractive index, n_D^{20}	1.4810	1.4821
Molecular weight	810	1100
Viscosity, Gardner-Holdt	A-A1	C
Iodine value, Wijs	183	173
Drying time, hours:		
Set to touch	2.7	2.5
Dust free	3.2	2.7
Hard dry	Not in 30 days	7 days

I claim as my invention:

1. A process of improving the drying properties of fatty oil having an iodine value of at least 120 which comprises heating said oil at about 100° C. to 250° C. in the presence of a peroxide compound containing a tertiary-alkyl peroxy radical.

2. A process of improving the drying properties of a fatty oil having an iodine value of at least 120 which comprises heating said oil at about 150° C. to 200° C. in the presence of about an added 0.5% to 10% by weight of a peroxide compound containing a tertiary-alkyl peroxy radical linked directly to another carbon atom than is present in said tertiary-alkyl group.

3. A process of improving the drying properties of a fatty oil having an iodine value above 120 which comprises heating said oil at about 100° C. to 250° C. in the presence of di-tertiary-butyl peroxide.

4. A process of improving the drying properties of a fatty oil of natural origin having an iodine value of at least 120 which comprises heating said oil at a temperature of about 100° C. to

250° C. while adding thereto about 0.5% to 10% by weight of a peroxide containing a tertiary-alkyl peroxy radical.

5. A process of improving the drying properties of sardine oil which comprises heating said oil at about 100° C. to 250° C. in the presence of 0.5% to 10% by weight of a peroxide containing a tertiary-alkyl peroxy radical.

6. A process of improving the drying properties of sardine oil which comprises heating said oil at about 150° C. to 200° C. in admixture with about an added 0.5% to 10% by weight of di-tertiary-butyl peroxide.

7. A process of improving the drying properties of soy bean oil which comprises heating said

oil at about 150° C. to 200° C. in the presence of di-tertiary-butyl peroxide.

8. A process of improving the drying properties of linseed oil which comprises heating said oil at about 150° C. to 200° C. in the presence of di-tertiary-butyl peroxide.

LEONARD P. WIEBE.

REFERENCES CITED

10 The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,219,862	Bradley	Oct. 29, 1940