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BODYING OF OIL BY HEAT

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The present invention relates to the treatment of glyceride oils preferably of the highly unsaturated or drying type and it has particular relation to the heat treatment of such oils in order to impart improved body thereto.

One object of the invention is to increase the rate of heat bodying of glyceride drying oils so that a satisfactory degree of bodying may be attained in a substantially shorter period of time than in conventional bodying operations.

A second object is to provide a process of the foregoing type in which the proportion of inhibitors inherent in most of the drying oils is reduced in amount.

A third object is to provide a bodied glyceride drying oil which is of improved color.

A fourth object is to provide a process of heat bodying oils by application of which fully bodied oils of exceptionally low acid value are attained.

A fifth object of the invention is to provide a process of bodying glyceride drying oils which involves the use of a promotor of bodying that combines permanently and advantageously with the oil and does not require treatment of the bodied oil in order to eliminate the promotor.

A sixth object is to provide a process of the foregoing type in which the promotor is required in relatively small amounts.

A seventh object is to provide a process of the foregoing type which is economical, simple and efficient of operation.

These and other objects of the invention will be apparent from consideration of the following specification and claims.

In the manufacture of coating compositions from glyceride drying oils such as linseed oil, soya bean oil, sardine oil and the like it is often desirable to increase the body or viscosity of the oil by subjecting it to heat in an appropriate container. The process admits of the use of substantially reduced quantities of the oil in the coating compositions and therefore admits of substantial increase in the amount of coating compositions that can be obtained from a small amount of oil. For these reasons, use of the process has greatly increased over the last several years of the World War during which period drying oils have been exceptionally scarce.

Usually the bodying operation is conducted at a temperature of about 280 to 315° C. which induces a partial polymerization of the oil with resultant thickening or increase of the viscosity. Also, the refractive index of the oil increases or decreases dependent upon the type of oil being bodied. Simultaneously there is often an in-

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crease of color or darkening which is objectionable and also an objectionable increase in the acid value of the oil presumably due to the breaking down of the glycerides during the bodying operation. The bodying operation could be continued to such degree as to induce the gelatin of the oil but usually it is preferred to stop the operation at an appropriate stage when a desired viscosity has been attained. This is easily judged by well recognized viscosity tests. In most instances, the bodying operation is conducted for a period of 6 or 8 hours dependent upon the specific requirements for the finished product, the individual characteristics of the oil being treated and such other factors. In any event, the bodying operation is relatively prolonged so that production from the apparatus is relatively limited and the consumption of energy in the form of heat is great.

In recognition of these facts, it has been proposed to incorporate into the oil promotors designed to increase the rate of bodying. Heretofore, no promotor satisfactory for the purpose has been discovered. In most instances the substances tried fell short in one or more of the following particulars:

(a) They were but feeble promotors.

(b) Too much promotor was required for the operation.

(c) The promotors were expensive to obtain.

(d) They were corrosive in their nature and were otherwise harmful so that special treatment of the oil was required in order to eliminate them at the conclusion of the bodying operation.

Mattiello in the text "Protective and Decorative Coatings," copyright 1943 by John Wiley and Sons, Inc. of New York, volume 3, page 29, describes the bodying of oil as "one of the most time consuming operations in the manufacture of paints and varnishes."

Ruthruff in "Chemical Industries," volume 58 (1946) page 245 states that "there will be a large and increasing demand for accelerators that really and materially accelerate the heat polymerization of drying oils."

The present invention involves as one feature the discovery that epoxy alkenes notably of the open chain, conjugate type are eminently suitable for use as catalysts in the heat bodying of glyceride oils. They are characterized by a capacity for effecting a sharp increase in the rate of heat bodying of the oil, small amounts are effective for the purpose and at the same time they seem to react permanently with the oil so that there is no necessity for treating the bodied

oil in order to eliminate the catalyst or promoter therefrom.

In the practice of the invention an appropriate oil for bodying is placed in a suitable apparatus such as a stainless steel kettle or other container having the necessary heating device, agitators, inert gas supply and meters or controls whereby the desired conditions of bodying can be accurately determined and maintained.

The main elements employed in the practice of the invention in the present case comprise:

(A) A drying glyceride oil adapted to be heat bodied.

(B) An open chain epoxy alkene in appropriate amount designed to promote bodying.

(C) A supply of an inert or non-reactive gas designed to be blown through the oil to be bodied during the warm up stage and shortly thereafter.

(D) An appropriate schedule for adding the epoxy alkene and for maintaining the bodying temperature.

ELEMENT A

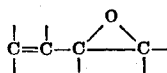
The drying glyceride oil

Oil suitable for heat bodying in accordance with the provisions of the present invention comprises any of the glycerides that it may be desirable partially to polymerize preliminarily to their formulation into paints and varnishes. These, of course, include linseed oil, soya bean oil, sardine oil and other oils susceptible of drying to form durable films upon a surface to be coated. The oils may be raw or unrefined or they may be preliminarily treated with alkali or acid in order to remove break and other objectionable constituents. The preliminary treatment of the oil with selective polar solvents by such methods as disclosed in Freeman Patents 2,200,390 and 2,200,391 to obtain selected fractions is also embraced within the scope of the invention.

ELEMENT B

The monoxide of a diene hydrocarbon

The promoter of bodying preferably is an epoxy alkene which usually is open chain. The essential molecular skeleton of the promoter includes the structure:



It will be appreciated that in this structure hydrogens or hydrocarbon radicals will be present to satisfy all of the valences indicated as radiating from the carbons of the 3,4 epoxy 1 butene skeleton. The group of promoters, therefore, includes 3,4 epoxy 1 butene, the simplest member of the class, methyl 3,4 epoxy butene from isoprene, dimethyl 3,4 epoxy 1 butene from butadiene, methyl 3,4 epoxy 1 butene from 1,3 pentadiene and other compounds of the class including the basic grouping. The promoter of bodying will be employed in amount varying over a considerable range dependent upon the type of oil being treated, the rate of bodying desired and other factors. Of course, in most instances it is desirable to keep the amount of promoter fairly low in order to reduce costs to a minimum and it is one of the important advantages of the present invention that the promoter can be employed in such amounts. Usually 1 to 5% of promoter, e. g. 3,4 epoxy 1 butene is satisfactory and the most preferred range is from about 2 to 4% by

weight based on the oil. Ranges of 1 to 10% of 3,4 epoxy-1-butene are contemplated.

ELEMENT C

The blowing of the glyceride oil with inert gas

During the preliminary period of warming the oil up to the bodying temperature it is desirable to blow the oil with an inert gas, that is a gas that does not react to a substantial extent with the oil being treated. This blowing operation may be conducted with nitrogen or carbon dioxide, or even with air, which although it may react with the oil to an extent does not do so to an appreciable degree during the period of preliminary warm up. An especially desirable inert gas mixture for use in the present invention is obtained by the combustion of butane. This gaseous product comprises nitrogen, carbon dioxide and probably other constituents where it is employed during the preliminary blowing. The final product is obtained in a state of exceptionally light color.

The blowing operation is found to be desirable since it tends to eliminate or at least to reduce in amount the natural inhibitors present in most of the glyceride oils and which tend if left in the oil to retard the subsequent polymerization reactions. The blowing operation should be conducted relatively vigorously in order to promote thorough contact of the oil with the inert gas, but of course, should not be so vigorous as to induce foaming or frothing or running over of the containers. The gases from the operation may be vented to the atmosphere. The bubbling or blowing operation may also be accompanied by mechanical agitation in order to promote uniform distribution of the gas in the oil and to secure uniformity of heating. The blowing operation may be initiated at or near the beginning of the warm up period and it is preferable though not essential that it be continued for a period, e. g. 5 or 10 minutes after the oil has reached its bodying temperature. In some instances a slow feed of inert gas may be maintained into the container throughout the period of bodying in order to insure an inert atmosphere above the bodying oil.

When the oil is sufficiently bodied it may again be blown relatively vigorously for a time while it is cooling in order to sweep out any volatile products residual in the oil or formed during the process of bodying. This latter operation is not essential but sometimes is of value.

ELEMENT D

The schedule of heating

The glyceride oil to be bodied, when introduced into the bodying apparatus, may be brought to a temperature as rapidly as possible consistent with maintenance of a reasonably uniform temperature (that is, the avoidance of local overheating or other objectionable effects). The preliminary heating operation may also be more prolonged if desired thus placing a lower load upon the heating coils or other heating devices employed with the apparatus. The amount of oil to be bodied also imposes a limitation upon the heating since large amounts of oil in a specific apparatus require more time to reach the bodying temperature than smaller amounts. Usually a preliminary warm up period of about 30 or 40 minutes up to 2 or 3 hours is permissible. During this time the oil will be brought approximately to bodying temperature. The preferred range for the operation is about 290 to 310° C.

though these values do not constitute the extreme limits. For example, temperature of bodying may be 270° C. up to about 350° C. Of course, a reasonably high lower limit is necessary in order to attain a satisfactory rate of bodying and the upper temperature should not be so high as to exceed the flash point of the oil or to cause undue darkening or decomposition of the oil.

As previously indicated, the oil during this preliminary warm up period is bubbled vigorously with an inert gas and the bubbling may be continued for a few minutes after the oil is sufficiently heated.

The promotor of bodying, e. g. 3,4 epoxy 1 butene, is introduced rather slowly into the bodying oil over a period beginning at or near the discontinuance of the vigorous bubbling with an inert gas. The compound should be added at such rate that a little will be free to reflux but there is not enough to cool the oil below the bodying temperature. In order to prevent any loss of 3,4 epoxy 1 butene or other promotor selected as herein suggested, the apparatus should be equipped with a suitable reflux condenser.

The bodying operation is continued until a satisfactory product is obtained as determined by conventional viscosity or other suitable tests. It is difficult to give any precise period of time for such operation since the latter will depend to a very large extent upon the degree of bodying desired in the finished product which will vary with individual requirements and also with different oils. For example, oils of one season may well be more difficult to body than oils of another and therefore require a longer period of bodying. Usually the oils can be bodied to a satisfactory degree within a period of about 1 to 3½ hours or thereabouts.

A glyceride oil bodied in accordance with the provisions of the present invention may be cooled at the conclusion of the heating period and is then suitable for formulation with pigments, dyes, resins, thinners and other compounding ingredients employed in the industry in the manufacture of the various coating materials. It is to be appreciated that the bodied oils can also be cooked with resins or plastics in the conventional varnish making operations.

The principles involved in the bodying of oils by the methods herein disclosed have been discussed. The following constitute specific examples illustrating the application of these principles:

EXAMPLE I

In a kettle equipped as described above, 1000 parts of alkali-refined linseed oil was heated to 302° C. with agitation and with a vigorous stream of inert gas passing through the oil. This required about 45 minutes. Then the condenser was attached to the system, the inert gas flow cut to a trace, and 3,4 epoxy 1 butene was added slowly. After one hour the oil had a body on the Gardner scale of N and after two hours a body of Z-1. The heat was shut off at the end of three hours, the condenser removed, and the oil again blown with inert gas as it cooled to 200° C. Thereafter the gas flow was stopped. A total of 34 parts of 3,4 epoxy 1 butene was added and a slight reflux existed at the end. The product was a light-colored oil having a Z-6 body, an acid number of 9.6 and was obtained in 98.5% yield. The latter was calculated on the total weight of oil and addition agent used.

EXAMPLE II

In a similar manner 1000 parts of linseed oil was treated at 310° C. with the same amount as in Example I of 3,4 epoxy 1 butene. The warm-up period was 50 minutes, the oil was held at 310° C. for 100 minutes and then cooled as before. The product was obtained in 97.5% yield and had an acid number of 14.5 and refractive index $n_D^{25^\circ}$ —1.4912.

EXAMPLE III

The use of a lower temperature is illustrated in this example. The same sized charge of alkali-refined linseed oil was heated, agitated, and blown as before. The temperature was raised to 293° C. in 40 minutes. 3,4 epoxy 1 butene was then added slowly until 5% was introduced. At the end of six hours the run was stopped and the oil blown and agitated as before during the first part of the cooling period. The product was obtained in 98.4% yield and had an acid number of 3.9, body over Z-6, and a refractive index $n_D^{25^\circ}$ —1.4912.

EXAMPLE IV

As an example of the effectiveness of this treatment, a control run was made without the promotor: 1000 parts of the same oil as in Example III was treated in the same manner in identical equipment. The warmup period was 40 minutes and the oil was held at 302° C. for 7.5 hours. The product had a body of only Z-1.5, an acid number of 12.8, a color matching 7 Hellige, and was obtained in 98.4% yield.

EXAMPLE V

As previously mentioned, the oils vary in their susceptibility to the blowing treatment. Oil from another crop was treated in similar equipment. A charge of 2500 parts of alkali-refined linseed oil was blown with inert gas for 2 hours during the warm-up period and then for 10 minutes longer at 302° C. The batch was held at this temperature for a total time of 3 hours 10 minutes, during which time 3.2% of 3,4 epoxy 1 butene was added. The batch was cooled as before. The bodied oil was obtained in 98.0% yield and had a body of Z-5, an acid number of 7.3, $n_D^{25^\circ}$ —1.4900, and a color of 6 Hellige.

EXAMPLE VI

It was pointed out above that other gases are effective in removing inhibitors from the oil. As an example, 2500 parts of alkali-refined linseed oil was heated in similar equipment to 295° C. and blown with air while the temperature rose to 302° and for 20 minutes thereafter. The air flow was shut off completely and 3,4 epoxy 1 butene was added slowly as before. The amount used was 3.3%. After 3 hours at 302° C., the heat was shut off and the oil again blown with inert gas for part of the cooling period. The product was obtained in 97.6% yield and had a body of Z-4, an acid number of 6.1, $n_D^{25^\circ}$ —1.4891 and a color of 7 Hellige.

EXAMPLE VII

A charge of 1000 parts of linseed oil was heated in similar equipment to 302° C. in 70 minutes. During this time and for 7 minutes after reaching this temperature, a vigorous stream of commercial carbon dioxide was passed through the oil. The flow of gas was reduced to a trace and 3.5% of 3,4 epoxy 1 butene added slowly. After 1.75 hours, the heat was turned off and the oil was swept with carbon dioxide for a short time. The product was obtained in 99.0% yield and had a

body of Z-3, an acid number of 3.9, n_D^{25} —1.4890 and a color of 8 Hellige.

EXAMPLE VIII

In a similar manner a charge of alkali-refined linseed oil was blown vigorously with commercial grade nitrogen during the warm-up period and then treated with 2.7% 3,4 epoxy 1 butene at 302° C. After 3.3 hours, the oil was cooled and blown with nitrogen. The product has a body of Z-3, an acid number of 6.4, n_D^{25} —1.4888 and a color of 5 Hellige.

EXAMPLE IX

Butadiene monoxide may also be used with other drying oils effectively. A soya bean oil extract was treated in the same equipment. Twenty-five hundred parts was heated and blown with inert gas until the temperature reached 302° C. The blowing was continued for 10 minutes, the gas flow cut to a trace, and 2.9% 3,4 epoxy 1 butene added. After 3.5 hours the batch was cooled as before. The product was obtained in 97.9% yield and had a body slightly over Z-1, an acid number of 11.2, n_D^{25} —1.4849, and a color of 7 Hellige.

EXAMPLE X

A charge of the same size of the same oil was treated in identical manner except no addition agent was used. The product, which was obtained after 7 hours at 302° C., was recovered in 98.3% yield and had a body of Z-1, an acid number of 16.2, n_D^{25} —1.4830, and a color of 7 Hellige.

It will be apparent that the monoxides of conjugate diene hydrocarbons herein disclosed produced a substantial acceleration of the rate of heat bodying of glyceride drying oils and therefore produce substantial economies in the operation of the bodying process. Moreover, the products are of improved color and acid value.

It would appear that the monoxides react with free carboxyls of oil acids in the bodied oil to form ester products. They also copolymerize with the oil. The monoxides, since they are combined as a part of the oil molecules, do not require further treatment of the oil in order to eliminate them from the bodied product.

The oils after bodying may be cooked with the conventional varnish makers gums and resins, such as ester gums or the like. They may be admixed with fillers and pigments, e. g. lithopone, titanium dioxide or other finely divided non-reactive material to form paints and varnishes. The compositions when spread, dry quickly to durable films.

Although the present invention has been described with reference to details of certain embodiments thereof it is not intended that such details shall be regarded as limited upon the scope of the invention except insofar as they are included in the appended claims.

I claim:

1. A process of heat bodying a glyceride drying oil which comprises admixing 1 to 10% of 3,4 epoxy 1 butene therewith and subjecting the mixture to bodying temperature until a desired degree of body is reached.

2. A process of heat bodying a glyceride drying

oil which comprises admixing 2 to 4% of 3,4 epoxy 1 butene with the oil and subjecting the mixture to a temperature of about 290–310° C. until desired body is reached.

3. A process of heat bodying a glyceride drying oil which comprises admixing about 1 to 10% of 3,4 epoxy-1 butene with the oil and subjecting the mixture to a temperature of about 290 to 310° C. until a desired degree of body is attained.

4. A process as defined in claim 1 in which the glyceride oil is linseed oil.

5. A process as defined in claim 1 in which the glyceride oil is soya bean oil.

6. A process of heat bodying a glyceride drying oil which comprises blowing the oil with a non-reactive gas to remove inhibitors inherent in the natural oil and at the same time bringing the oil up to the bodying temperature, then slowly adding a small catalytic amount of 3,4 epoxy 1 butene to the oil while it is maintained at the bodying temperature and maintaining the oil at the bodying temperature until the desired degree of body is attained.

7. A process of heat bodying a glyceride drying oil which comprises heating the oil to a temperature of about 290 to 310° C. and adding thereto 2 to 4% of 3,4 epoxy-1 butene and maintaining the oil at said temperature until it is sufficiently bodied.

8. A process of heat bodying a glyceride drying oil which process comprises blowing the oil with a non-reactive gaseous medium to remove inhibitors from the oil while at the same time heating the oil, continuing the operation until the oil has attained bodying temperature, then adding about 1 to 5% 3,4 epoxy-1 butene to the oil and continuing to heat the oil until it is sufficiently bodied.

9. A process of heat bodying a glyceride drying oil which comprises admixing 1 to 10% of a 3,4 epoxy 1 alkene in which the alkene group contains 4 to 6 carbon atoms with the oil and subjecting the mixture to a bodying temperature until desired body is reached.

10. A mixture of a drying glyceride oil and 1 to 10% of 3,4 epoxy 1 butene which is adapted to body when heated to a temperature of 290 to 310° C.

11. A process of heat bodying a glyceride drying oil which comprises admixing a 2 to 4% of 3,4 epoxy-1 alkene in which the alkene group contains 4 to 6 carbon atoms with the oil and subjecting the mixture to bodying temperature until desired body is reached.

12. A process as defined in claim 9 in which the bodying temperature is within a range of 270 to 350° C.

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REFERENCES CITED

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

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