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PRODUCTION OF SUPERBODIED OILS

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This invention relates to homogeneous, gel particle-free oils derived from unsaturated fatty acid polyesters, and to an improved method for their manufacture at atmospheric pressures. More specifically, the invention relates to the production of such fatty oils characterized by viscosities above 14 minutes, herein called "super-bodied oils." It is to be understood that the viscosity value referred to herein is based upon the time required for an air bubble to travel the length of a standard Gardner varnish viscosity tube under standard temperature conditions (77 degrees F.).

Conventionally, heat-bodied oils having viscosity values above 14 minutes are usually lacking in homogeneity, and almost invariably gel upon age to a solid state. Super-bodied, gel-free, homogeneous oils have heretofore been prepared by heat-bodilying fatty oils at reduced pressures to produce viscosities above the 10 to 14 minute range. The vacuum method of super-polymerizing fatty oils inherently has the mechanical problems of vacuum operations, high losses and longer periods of time to produce a specified viscosity. This is especially true when viscosities above the range mentioned as critical are desired.

So far as is known, there are no unusual difficulties encountered in producing oils of 8 to 10 minutes or less in viscosity from drying oils except that by conventional procedure an unduly long time is required. However, it is usual to find with ordinary bodying procedures, after viscosities of about 14 minutes have been produced, the homogeneous appearance of the viscous oil is lost, gel particles are incipient or actually form, and the oil when poured in a fine stream as from a vial, may reveal a string-like characteristic, an initial stage in the transformation from a sol to a gel phase. Varnish makers know when this condition is first observed that the prompt addition of either fatty acids or rosin to the varnish or oil often saves the cook from gelation or "monkeying." Complete gelation at bodying temperatures, after incipient gel formation, occurs with great rapidity. Fast action on the part of the oil cooker is necessary to arrest the change from the sol to the gel phase. Such arresting of polymerization is commonly referred to by varnish makers as a "checking operation" or a "check" and has for one primary purpose a rapid reduction in the temperature of the batch. In cases where rosin and/or fatty acids are the checking means, it is well known that these acidic materials possess the additional quality of dispersing the primary gel particles which have begun to form in the varnish or oil.

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Another practice oil in the art in checking is to direct a stream of water on the outside of the kettle, as from a hose, after cutting off the source of heat. Occasionally, more adventurous varnish-makers will purposely direct water into the batch, a dangerous practice which effectively reduces the temperature through heat transfer to the water and the consequent formation of steam. In general, this practice is condemned and so far as is known there has been no record of observations of the effect of such a procedure upon oils and varnishes so treated. It is obvious that one would not normally resort to such drastic cooling methods unless the end in mind was to reduce the temperature quickly to inhibit greatly the rate of reaction in the kettle. To replace a gelling batch of oil or varnish on the fire or to continue or to resume heating at such a critical stage would be contrary to all established practice in the art.

To clarify the concept of viscous oil stability, the following test used by the varnish maker may be helpful. When a varnish or oil-maker is in the process of cooking a batch, small samples are removed periodically from the batch and in some cases are further reduced with solvents to a specified solvent-solids content, the sample placed in a standard glass vial or tube leaving a small free air space in the tube. When cooled to standard temperature conditions (e. g., 77 degrees F.), the observer will clock the time required for the air space in the test tube to travel from the bottom to the top of the tube following its quick inversion.

Through experience, the varnish maker has learned if the small bubble leaves a "tail" or a "tit" in the oil as it progresses from the bottom to the top of the tube, that said oil or varnish will probably be unstable with age. That is, polymerization is likely to proceed even after the oil or varnish has been completed and stored. Polymerization may proceed to a point where the product will no longer pour, and the oil will resemble a jelly. It is common experience that oils bodied at atmospheric pressures or above by conventional means to about 10 to 14 minutes may upon test, evidence this peculiar "tail" in the bubble, and possess uncertain shelf life.

One of the objects of the present invention is to provide a new and improved process of producing super-bodied homogeneous oils at atmospheric pressures or above.

Another object is to produce new and improved super-bodied oils. Other objects will appear hereinafter.

The ability to produce super-bodied oils at atmospheric pressures and above in accordance

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with the present invention has been made possible through the observation that oils polymerized to the point where gel particles are observable, and heterogeneity between solid and fluid phases in the oil is initiated, can be held a longer period of time at bodying temperatures, the initial gels formed dispersed, and additional gelation prevented by blowing the latently gelling mass with steam.

The process of the present invention for manufacture of homogeneous, super-viscosity oils consists essentially of bodying a fatty oil to a stage of latent or incipient gelation at atmospheric pressures or above, checking the polymerization rate by blowing the fatty oil with steam, and, after the initial checking, again holding the hot oil at or near bodying temperature while passing steam through the heated oil. The preferred method is to heat-body a semi-drying oil by the methods of my co-pending abandoned application, Serial No. 34,809, filed June 23, 1948, to the point of latent gelation (e. g., about 5 to 10 seconds "cure" point) at which time the viscosity of the oil is indeterminant due to the presence of latent gel particles, and thereafter check the polymerization and blow the oil with steam.

While it is not essential to the production of superpolymer oils to use the bodying methods given in my co-pending application, Serial No. 34,809, filed June 23, 1948, by doing so considerable advantages accrue. It is often possible to body oils by standard means to the point of incipient gelation as a starting point for the manufacture of super-polymer oils and at the point where this process is initiated, said oils having indeterminant viscosities of about 10 to 14 minutes. Soya bean oils or other oils having iodine values classifying them in the semi-drying range cannot be bodied to the point of gelation by standard practice. With some oils, e. g., semi-drying oils, it is essential that catalytic means be employed to body them to the required initial degree to achieve the higher degree of viscosity of the process herein disclosed.

The practice herein disclosed, to return a gelling batch to the fire or to maintain the temperature of the oil after adding water to the hot batch to form steam, or blowing the hot batch with steam directly after the first gelation symptoms without removal from the fire, is a unique procedure based on the discovery that steam acts as a dispersant for gels formed and an inhibitor against further localized gelation within a varnish or oil batch.

It is surprising that passage of steam through the batch allows continued heating at bodying temperatures even after gelation has become visibly initiated, and that uniform bodying will thereafter continue for a sufficient time to produce oils having Gardner tube viscosities as high as an hour or more, characterized by freedom from localized over-polymerization or gel particles and by an unbroken, smooth flow from a spade or paddle. The resultant oils also possess a practical shelf life. It has been specifically found that heating may be continued at near-bodying temperature levels to increase the viscosity of the oil and yet maintain a smooth, homogeneous, gel particle-free product provided the sparge or blowing with steam is continued. By steam treatment after first heat-bodying in a conventional manner, it has been found possible to produce oils with viscosities in excess of 14 minutes. If desired, the initial bodying

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methods disclosed in the previously mentioned co-pending application may be used.

If the super-bodied oils are made by the process herein described, it is possible to produce oils of one hour, more or less, in viscosity yet having complete homogeneity, freedom from gel particles, and as far as is known, excellent stability upon storage.

In practice, after bodying to incipient gelation at a temperature of 500 degrees F. to 625 degrees F. and checking with steam, the temperature is held within or near the bodying range, and the steam blowing is continued at said temperature until a viscosity greater than 10 to 14 minutes and preferably above 20 minutes has developed, and the oil cooled by additives such as additional oil, rosin or other compatible resin or by natural or accelerated cooling to below bodying temperature to inhibit further polymerization. The point at which the polymerization is to be stopped, i. e., the temperature reduced to below the bodying temperature range, is preferably followed by means of "cure" point values as these values have been found to give accurate control means. The cure value should not be allowed to go below 5 to 10 seconds as at this point gelation of the oil is imminent.

The "cure" point is a means of observing the progress of a polymerization reaction. Measurement is made by exposing a drop of the reactant to the polished surface of a metal slab maintained at a constant temperature of 200 degrees C. (392 degrees F.). Immediately upon exposure of the drop to the surface, it is spread out over the largest possible area with a pointed metal tool. At the moment of application of the drop to the plate, a timer is started. The film is continuously spread until gelation occurs, and the time required to allow gelation of the film noted. The elapsed time, from application of the drop to the "cure" plate until gelation of the film is the "cure." The smaller the "cure" value, the nearer gelation is the reactant. Five to 10 second cures are indicative of latent or incipiently gelling reaction masses.

It has been found that such a product will remain stable, smooth and homogeneous, free of gel particles, and will not continue to polymerize or body appreciably after it has been cooled to room temperatures. The stability of super-high viscosity oils prepared by the above process is demonstrated by the absence of a "tit" or "tail" in the bubble when determining the viscosity in selected tubes or vials. As before mentioned, this "tail" formation has long been known as a warning sign of instability and said indication when present gives notice that gelation upon storage is likely.

The invention may be illustrated by the following examples in which the quantities are stated in parts by weight.

Example I

8,000 parts varnish maker's linseed oil
40 parts anthraquinone
250 parts linseed fatty acid

The linseed oil was heated in a varnish kettle equipped with a blow ring along with a light carbon dioxide blow to 585 degrees F., adding the anthraquinone meanwhile. At 585 degrees F. a flow of sulfur dioxide gas was also bled into the hot oil. The exothermic reaction raised the oil temperature to 600 degrees F. at which point the temperature was maintained and the mixed gas blow continued for approximately 2 hours.

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After this period of time the viscosity of the oil was between 25 to 35 minutes (i. e., incipient gelation with a "cure" of from 5 to 10 seconds). The batch was checked from further polymerization by spraying water into the batch causing a steam blow which was continued for one-half hour and the temperature thereby reduced to 500 degrees F. The mixed gas blow was again started and continued until incipient gelation of the batch was again noted by observation of the tendency for gel particles to form. The batch was rapidly cooled below bodying temperatures partly through adding 250 parts of linseed fatty acids. The cooled oil had a viscosity of one hour and was free of all semblance of gel particles.

This example illustrates the bodying of linseed oil, checking the batch with steam at incipient gelation and forming a super-polymerized oil having a viscosity in excess of 15 minutes, yet free from gel particles.

Example II

8,000 parts alkali refined soya bean oil
35 parts beta carboxyanthraquinone

The oil and catalyst were heated to about 600 degrees F., meanwhile maintaining a light carbon dioxide blow through the bulk of the batch. Upon reaching the temperature of 590 degrees F. to 600 degrees F., the sulfur dioxide gas was turned on and bled through the batch. After 5 hours at 600 degrees F., the oil was found to have attained a "cure" point of 10 seconds.

The batch was pulled off the fire and checked by adding water cautiously until the temperature was reduced to 480 degrees F.

Upon cooling a sample of the oil to room temperature, it was found to have a final viscosity of 9 minutes.

This example illustrates the result obtained by checking with water as is sometimes done by the trade.

Example III

The batch made as in Example II was again pulled onto the fire, the temperature brought up to 500 degrees F., the oil held for 15 to 20 minutes at 500 degrees F. with a light steam blow. The batch was thereafter cooled by the addition of 350 pounds of rosin. After rapid cooling of the batch an oil of 15 to 20 minutes viscosity was obtained, free of gel particles, and homogeneous in character.

Example IV

7,000 parts varnish maker's linseed oil
35 parts beta carboxyanthraquinone
350 parts rosin

The varnish maker's linseed oil was heated to 400 degrees F., and the 35 parts of beta carboxyanthraquinone were then added, meanwhile a light blow with an inert gas was maintained through the oil as it was further heated to 575 degrees F. At the latter temperature sulfur dioxide gas was also bled into the batch. The temperature increased to 590 degrees F. and was held at this temperature meanwhile maintaining the mixed gas blow for a little more than two hours. The oil at this time began to show evidences of more than one phase, or lack of homogeneity (e. g., incipient gelation), and the gases were shut off and steam admitted through a blow ring in the kettle through the hot oil. The fire was cut and the batch held at 525 degrees F. for 15 to 20 minutes while the steam

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blow was continued. The batch was removed from the fire, 350 parts of rosin added to assist cooling and check polymerization and the batch further cooled by water being directed on the outside area of the kettle. Upon reaching room temperature, an oil having a viscosity in excess of one hour was obtained. The oil was homogeneous and free from gel particles. As far as is known, stable oils of this viscosity have not heretofore been produced at atmospheric pressures.

Example V

7,000 parts alkali refined linseed oil
290 parts refined tall oil

The linseed oil was weighed into a usual varnish kettle equipped with a blow ring through which a light stream of carbon dioxide was passed, mainly to envelop the exposed surface of the oil to an inert atmosphere.

The batch was taken up to 590 degrees F. and maintained at this temperature plus or minus 10 degrees F., for from 8 to 10 hours, the time being determined somewhat by the quality of the oil and the ability to control the temperature at the point desired. After the oil had been held at the bodying temperature for this length of time, incipient gelation of the batch was observed. The carbon dioxide gas was shut off, the fire lowered under the batch, and steam blown through the hot oil by means of the blow ring reducing the temperature to 500 degrees F., and this temperature was maintained and the steam blow continued for 30 minutes, whereupon 290 parts of an acid refined tall oil were added and the batch rapidly cooled to below 350 degrees F. by directing a stream of cold water on the outside area of the kettle.

The resulting bodied oil was free from objectionable gel particles and was smooth and homogeneous having a viscosity in excess of one hour.

This example illustrates the added time required to body a linseed oil to incipient gelation without aid of added catalysts (see Example IV for comparison), and the method of blowing with steam to disperse incipient gelation, and further super-bodying of the oil with a final check upon polymerization rate being made with a mixture of rosin acids and fatty oil acids as they occur in tall oil, a by-product recovered from the manufacture of paper.

It is within the scope of the examples illustrative of my method that resins may also be incorporated in the oils at some time in the processing steps preferably after the oil has been super-bodied. It may be desirable in some instances to include rosin esters or other resins in the oil prior to the bodying operation, or it may be found more expedient to use additional amounts of resins as checking means after the oil has been suitably bodied.

Other means of rapid cooling after steam blowing of the oil while the temperature is maintained for the brief period following the incipient gelation stage of the oil are useful in lieu of the addition of the specific agent shown in the foregoing examples. If the kettles are heated by means of a liquid heat transfer medium (e. g., Dowtherm) cold or cool liquid heat transfer medium may be blended with the hot medium in the jacket to force cool the completed batch in the kettle. An alternative method of cooling is to continue to blow the batch with steam after shutting off the source of heat to the kettle of bodied oil, and continuing the steam blow until the temperature has been reduced sufficiently

to effectively retard polymerization. Another method which can be used (with due precaution due to dangerous consequence should negligence occur) is to spray a fine mist of water upon the surface of the hot oil thus extracting the sensible heat from the kettle until the temperature has been sufficiently reduced to arrest reaction.

The term "quinone" is employed in accordance with the usage in my previously described co-pending application to cover an organic, aromatic, unsaturated 1,3 in respect to both carbon and oxygen, cyclic di-ketone containing at least six carbon atoms. The quinone compounds may be partially substituted, although the non-substituted quinones are preferred. Certain of these may be derived through oxidation of multiple ring compounds, e. g., phenanthrene.

Some quinones will sublime out of the unsaturated fatty acid polyesters at temperatures used for bodying oils, and it is well known that a blowing operation will hasten the removal of such volatile material. For this reason the quinone is preferably selected according to the bodying temperature to be used. Between 500 degrees and 565 degrees F. anthraquinone or beta-chloroanthraquinone are preferred, while at higher temperatures such as 565 degrees to 625 degrees F. anthraquinone carboxylic acid or retene quinone are advantageous because of their lower vapor pressures at higher temperatures.

The catalytic amount of quinone employed is preferably within the range of .01% to 1% by weight of the oil treated.

It will be understood that the foregoing reference to quinones relates to the preparation of starting materials for the purpose of the present invention, especially where the starting materials are derived from non-conjugated drying oils having an iodine value greater than 120.

The invention is hereby claimed as follows:

1. A process for the manufacture of super-bodied fatty oils free from gel particles and above 14 minutes in viscosity, which comprises heat-bodying an unsaturated fatty acid polyester oil to incipient gelation within a 500 degrees F. to 625 degrees F. temperature range, blowing the said polyester with steam while maintaining said temperatures until the viscosity is again more than 14 minutes; and thereafter cooling the hot mass to inhibit further bodying action.

2. A process for the manufacture of homogeneous, gel particle-free fatty oils more viscous than heretofore producible at atmospheric pressures and above, which comprises heat-bodying an unsaturated fatty oil acid polyester to incipient gelation within a 500 degrees F. to 625 degrees F. temperature range, dispersing the incipient gel by blowing with steam while maintaining said bodying temperatures until the viscosity level surpasses that attained prior to the start of the steam blow, and thereafter rapidly cooling the oil to below bodying temperature to inhibit further bodying action.

3. A method of manufacturing viscous homogeneous fatty oils free of gel particles, not heretofore producible at atmospheric pressures or above, which comprises heat-bodying an unsaturated fatty acid polyester oil to latent gelation within a 500 degrees F. to 625 degrees F. temperature range at pressures which are at least atmospheric, dispersing the latent gel with steam while maintaining oil bodying temperatures and thereafter rapidly cooling the bodied oil to below bodying temperature.

4. A method of manufacturing viscous homogeneous gel particle-free fatty oils more viscous than heretofore producible at atmospheric pressures and above, which comprises catalytically heat-bodying an unsaturated fatty acid polyester oil to latent gelation within a 500 degrees F. to 625 degrees F. temperature range at pressures which are at least atmospheric, dispersing the latent gel by blowing with steam while maintaining bodying temperatures until the viscosity surpasses that attained prior to the steam blow, and thereafter cooling the oil and checking the polymerization rate.

5. A method of manufacture of an oil characterized by a higher viscosity than heretofore produced at atmospheric pressures and above, homogeneous and free from gel particles, which comprises heat-bodying an unsaturated fatty acid polyester oil in the presence of a quinone and sulfur dioxide until the viscosity becomes indeterminate, checking the latently gelling oil by blowing with steam until a viscosity at least above 14 minutes has been regained while maintaining a temperature of from 500 degrees F. to 625 degrees F., and thereafter cooling the said super-bodied fatty acid polyester oil to below bodying temperatures.

6. A method of manufacture of an oil characterized by a higher viscosity than heretofore produced at atmospheric pressures and above, homogeneous and free from gel particles, which comprises heat-bodying an unsaturated soya bean acid polyester oil in the presence of a quinone and sulfur dioxide until the viscosity becomes indeterminate, checking the latently gelling oil by blowing with steam until a viscosity at least above 14 minutes has been regained while maintaining a temperature of from 500 degrees F. to 625 degrees F., and thereafter cooling the said super-bodied soya bean acid polyester oil to below bodying temperatures.

7. A method of manufacture of an oil characterized by a higher viscosity than heretofore produced at atmospheric pressures and above, homogeneous and free from gel particles, which comprises heat-bodying an unsaturated linseed acid polyester oil in the presence of a quinone and sulfur dioxide until the viscosity becomes indeterminate, checking the latently gelling oil by blowing with steam until a viscosity at least above 14 minutes has been regained while maintaining a temperature of from 500 degrees F. to 625 degrees F., and thereafter cooling the said super-bodied linseed acid polyester oil to below bodying temperatures.

8. A method of manufacturing viscous fatty oils, free of gel particles, which comprises heat-bodying an unsaturated fatty acid polyester oil until latent gel particles become incipient within a 500 degrees F. to 625 degrees F. temperature range, steam blowing the said oil by spraying with water and maintaining said temperature until the viscosity surpasses that developed prior to the steam blow, and adding rosin thereafter to cool and inhibit further bodying action.

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REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
1,087,064	Kaempfe	Feb. 10, 1914
1,745,877	Thurman	Feb. 4, 1930