Jan. 23, 1945. R. A. CARLETON 2,367,666

METHODS AND MEANS FOR TREATING GLYCERIDE OILS OF THE UNSATURATED ESTER TYPE

Filed March 13, 1941 6 Sheets-Sheet 1

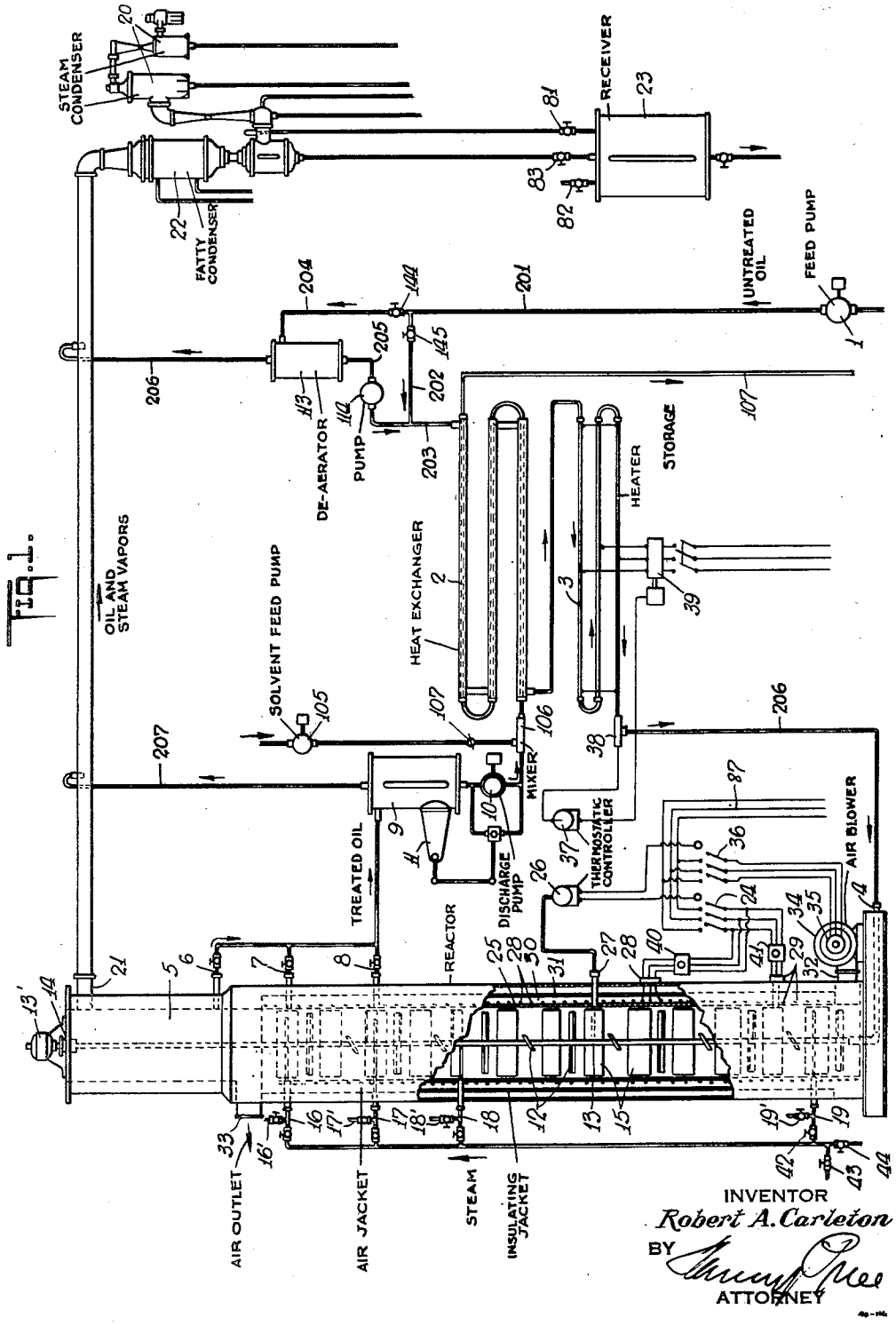


Fig. 1.

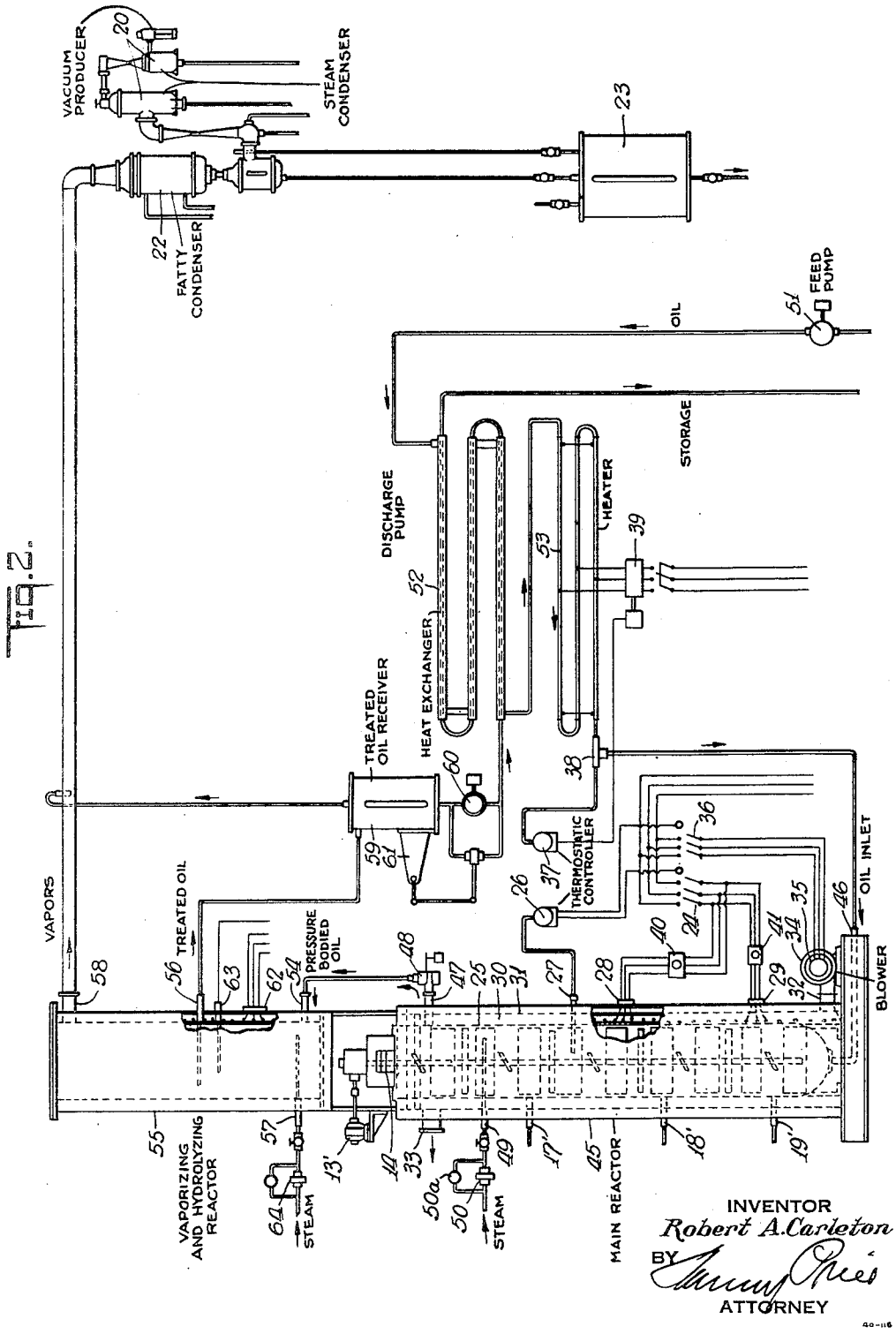
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METHODS AND MEANS FOR TREATING GLYCERIDE OILS OF THE UNSATURATED ESTER TYPE

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Fig. 2.



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METHODS AND MEANS FOR TREATING GLYCERIDE OILS OF THE UNSATURATED ESTER TYPE

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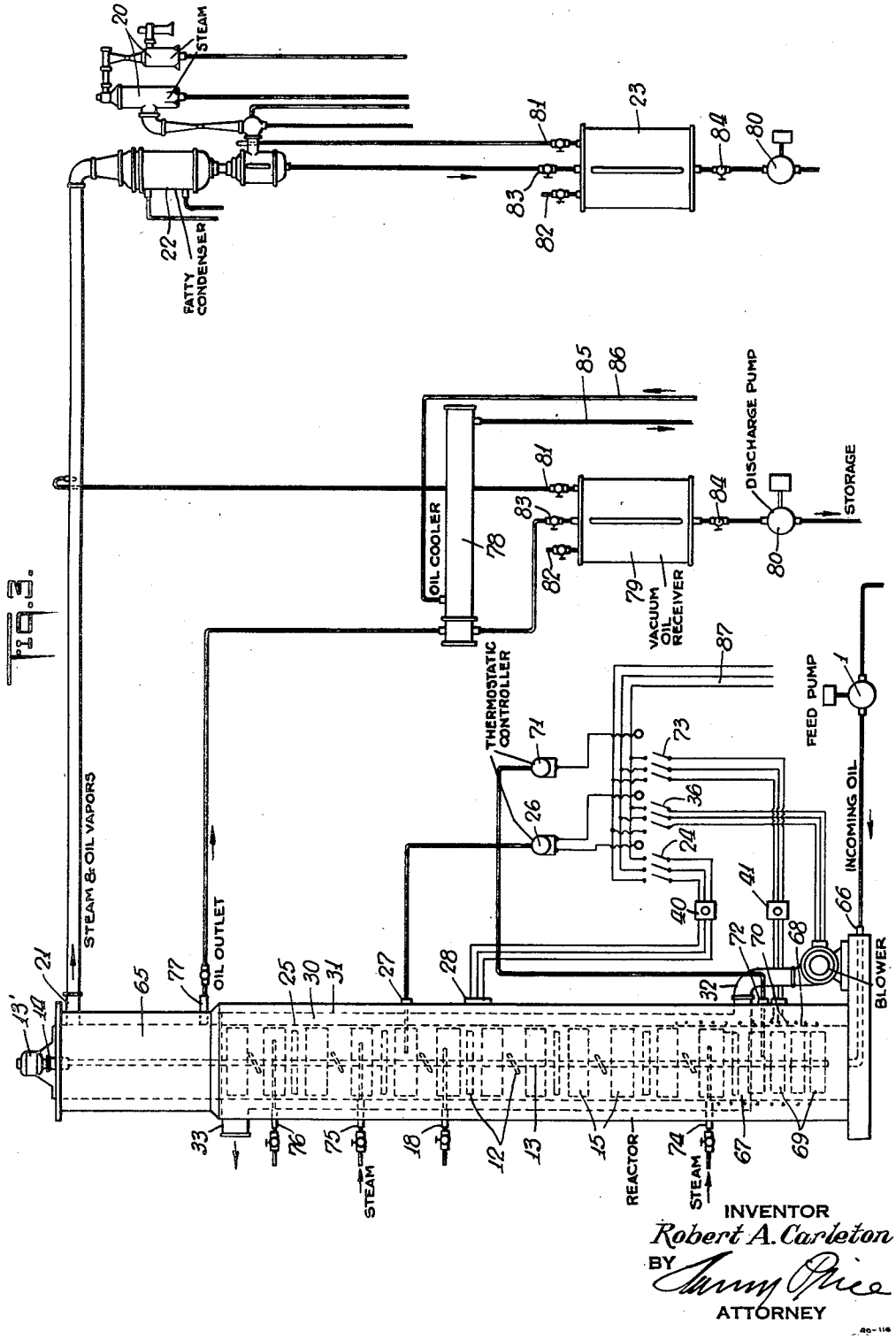


Fig. 3.

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METHODS AND MEANS FOR TREATING GLYCERIDE OILS OF THE UNSATURATED ESTER TYPE

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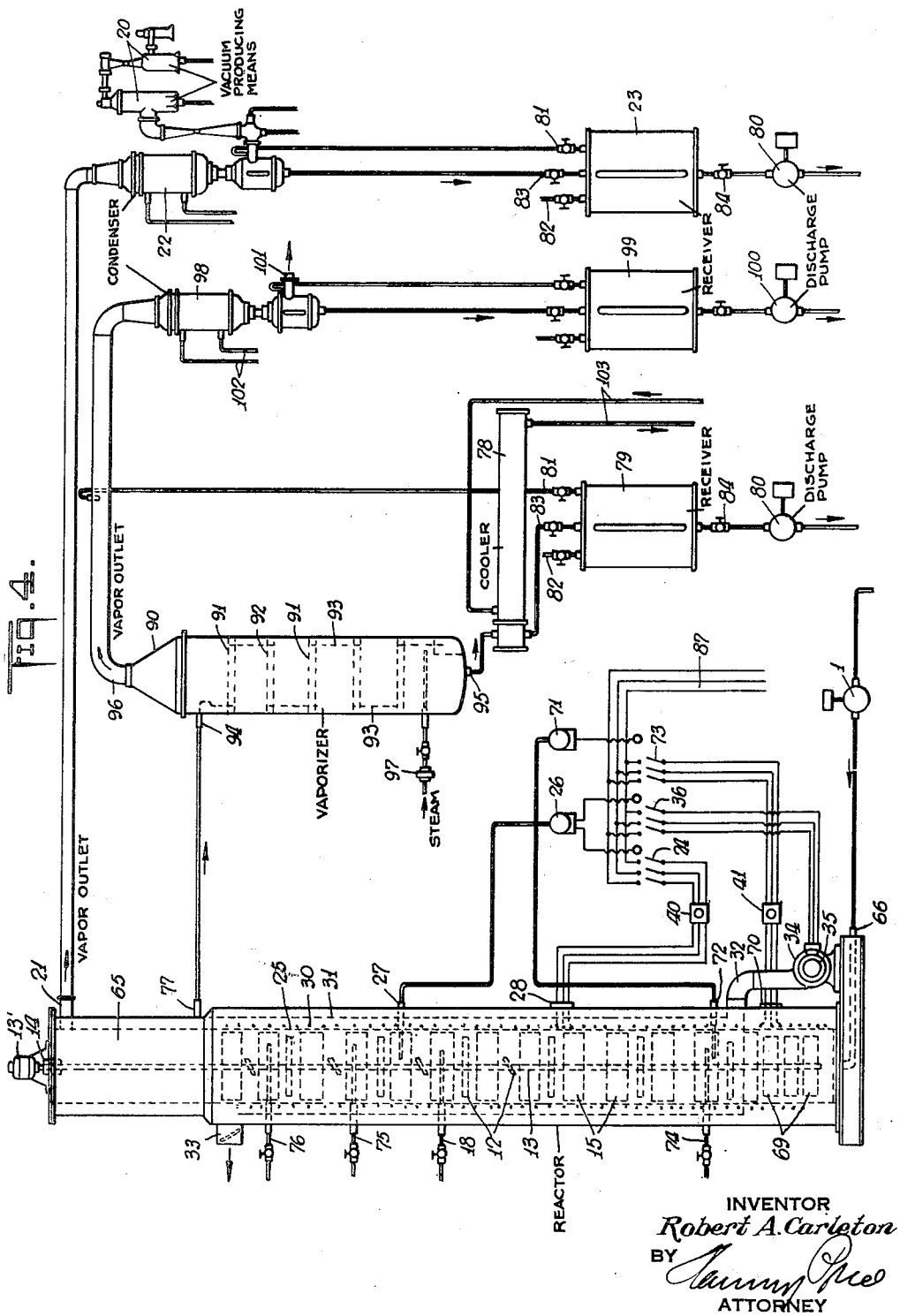


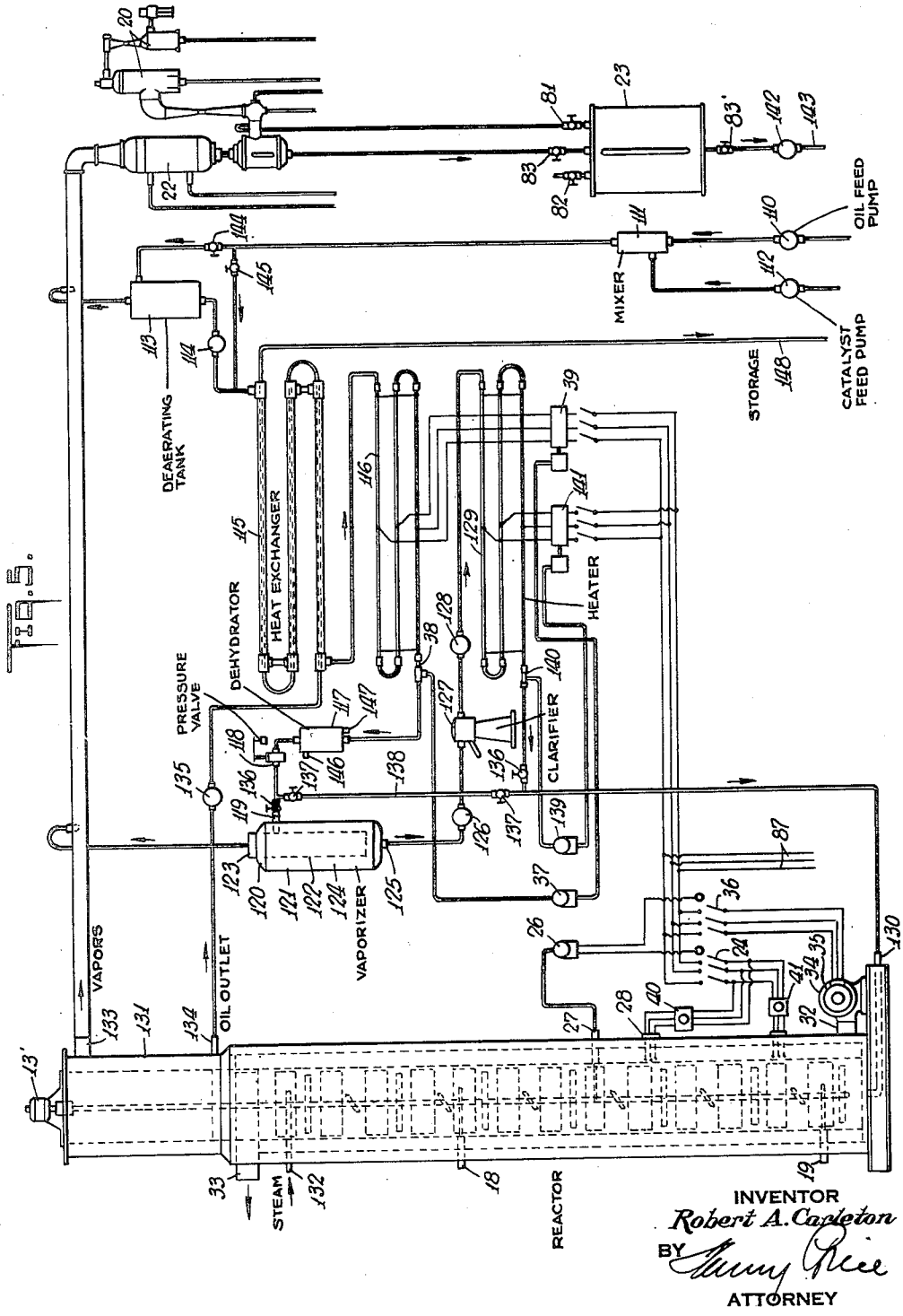
FIG. 4.

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Fig. 6.

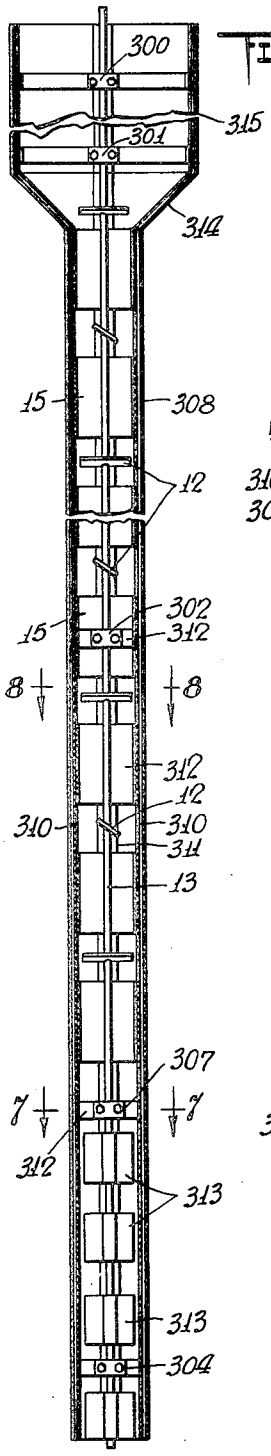


Fig. 7.

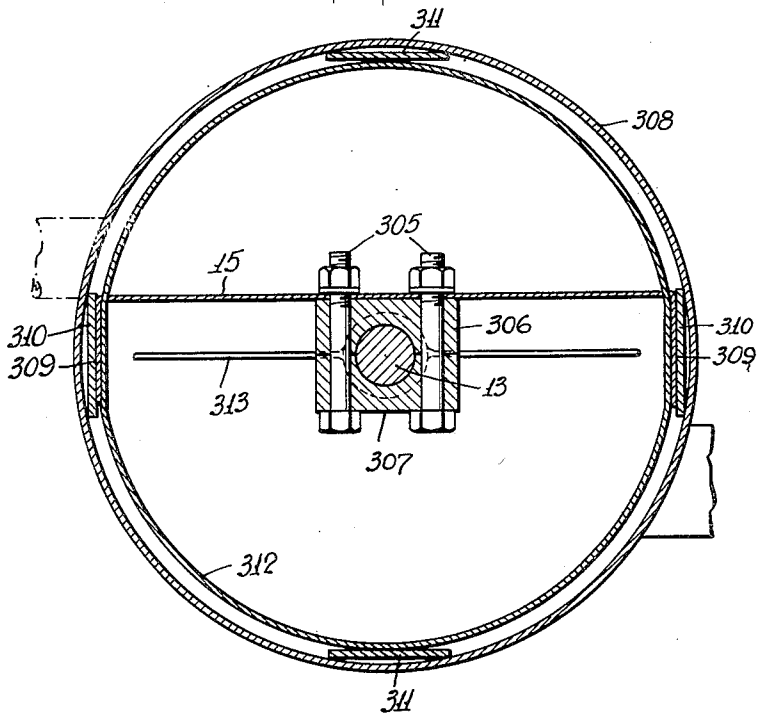
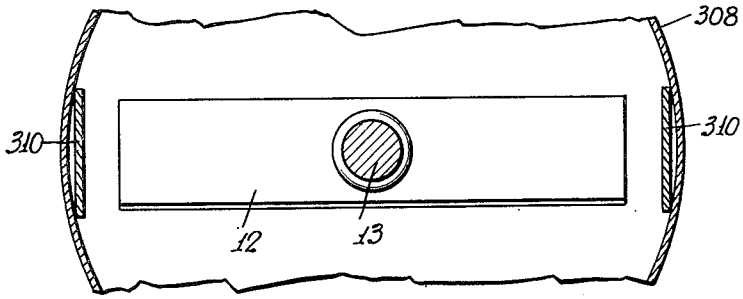


Fig. 8.



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UNITED STATES PATENT OFFICE

2,367,666

METHODS AND MEANS FOR TREATING GLYCERIDE OILS OF THE UNSATURATED ESTER TYPE

Robert A. Carleton, New York, N. Y.

Application March 13, 1941, Serial No. 383,184

21 Claims. (Cl. 106—220)

This invention relates to improvements in methods and apparatus for treating drying and semi-drying oils to give these oils more desirable drying and better film forming characteristics.

In the manufacture of paints, varnishes and similar coating materials, drying oils such as China-wood, linseed, Perilla and fish oils are commonly used for their film forming properties. These drying oils are also used in the manufacture of linoleum and other products in which they serve as a binder.

These drying oils have a relatively high degree of unsaturation and are characterized by their property of drying to hard, elastic and tough adherent film with absorption of oxgen from the air.

Generally the drying oils that have the most desirable drying properties are those having the greatest degree of unsaturation and ability to absorb oxygen, as is indicated by their high iodine value, and the best drying oils are regarded as those having more than 16 carbon atoms in the molecule and an iodine value above 140. Among the drying oils, China-wood, linseed, Perilla and fish oils are considered the most valuable.

China-wood oil is particularly valuable due to the hardness and the resistance of its film to hot water and alkaline cleansing solutions as contrasted to linseed, fish and other oil films which tend to soften and turn white when so exposed.

As compared to China-wood oil, most of these drying oils contain substantial amounts of saturated or non-drying compounds, such as glycerides of myristic and palmitic acids, together with compounds of the oleic type, having a relatively low iodine value, which disadvantageously affect the drying properties.

These saturated and low iodine value compounds in an oil for paints, varnishes and similar purposes act as an inert material or impurity, and prevent or retard the formation of the desired dry, hard, elastic skin upon drying. These saturated or non-drying compounds in the oil form a sticky gummy mass, which is interspersed with the compounds that dry to a hard film. The greater the percentage of these contaminating non-drying compounds in the mixture, the more tacky, soft and less desirable is the film.

China-wood oil, for example, which has most desirable drying characteristics, has but 6 to 10% of saturated and semi-saturated compounds. Linseed oil, on the other hand, contains from 12 to 18%, Perilla oil from 18 to 23% and sardine and menhaden fish oils contain from 23 to 35% of such non-drying compounds.

There are also many readily available, relatively inexpensive oils having large amounts of unsaturated components with drying properties, which cannot be readily utilized for drying oils because of their high proportion of saturated or semi-saturated components, cottonseed, corn and similar oils which contain above 35% of such non-drying constituents being examples of this class.

It is among the objects of the present invention to provide improved methods and means for treating drying and semi-drying oils so as to eliminate or decrease the amount of relatively non-drying compounds therein, either of a saturated or semi-saturated nature, whereby it is possible to produce from oils containing relatively large quantities of saturated or semi-saturated compounds and therefore having relatively poor drying properties, high grade oils which will form highly desirable dry, hard elastic skins not tending to be tacky or sticky and not tending to soften or whiten or become porous when exposed to hot water or alkaline cleansing solutions.

Another object of the present invention is to provide a process for converting relatively low grade drying oils, as for example of the nature of linseed, fish, soya bean, sunflower and similar oils, into relatively high grade drying oils where they will be able to compete with and have desirable drying and film forming characteristics approaching those of China-wood oil.

I have discovered that after the desired unsaturated glycerides have been converted to relatively high molecular weight compounds by polymerization and condensation with heat, the relatively low molecular weight saturated glycerides may be readily hydrolyzed to their fatty acids and removed from the oil by distillation. The oil is thereby converted from an inferior drying product to one having very desirable drying characteristics.

This polymerization and condensation or so-called thickening or bodying reaction of these unsaturated oils consists of a rearrangement or combination of the molecules to form molecules of higher molecular weight, with the double bonds being rearranged and connected with other bonds, resulting in a ring structure with substantial increase in speed of oxidation and drying ability.

The heat reaction results in a substantial increase in molecular weight of the unsaturated components in the oil, linseed oil for instance increasing from an initial value of 875 or less to 2300 or more, whereas the molecular weight of

the saturated glycerides remain substantially at their initial low value of 725 to 850.

The first or polymerizing reaction at high temperature is generally effected within a relatively short period of time, and within the conventional temperature range of about 540° F. to 700° F. for the polymerization of drying and semi-drying oils. For instance, when treating a linseed oil at a temperature of 625° F., its iodine value was reduced from an initial of 183 to a substantially constant value of 105 within a period of ten minutes, during which time its increase in viscosity was relatively small or from four to twelve poises.

The second or condensation reaction extends over a considerably longer period of time. For instance, upon continuing the foregoing heat treatment with the linseed oil for a period of forty minutes, there resulted an increase in molecular weight from 860 to 1975, with increase in viscosity from 12 to 290 poises, without substantial change in iodine value. The saturated non-drying oils in the compound were substantially unchanged.

It has been found that the saturated compounds of relatively low molecular weight remaining in the oil after the heat bodying reaction, may be readily selectively hydrolyzed and converted to their corresponding fatty acids having molecular weights of 250 to 285, which may then be vaporized at a relatively low temperature together with other volatile non-drying saturated or reduced glyceride contaminates and readily removed from the oil by vacuum and/or steam distillation, without substantial change or effect on the higher molecular weight bodied unsaturated quick drying compounds.

For example, I have found that by subjecting a certain sardine oil having an iodine value of 182 to appropriate treatment in accordance with my invention to decompose and remove about 30% by weight of the more saturated compounds from the oil by distillation, the resulting drying oil product has an equivalent iodine value of 237 and dries to a hard, tack free, elastic film at least as highly resistant to boiling water as China-wood oil and in less than one-fifth the time required by the original untreated sardine oil.

The aforesaid treatment will also advantageously affect any relatively low molecular weight mono- and di-glycerides which may be formed during the bodying reaction, which have relatively poor drying and film forming characteristics, the high temperature condensive reaction resulting in substantial esterification and re-combination with other unsaturated molecules with resulting improvement in their drying and film forming characteristics.

Similar results have also been offered by thus removing the saturated or relatively non-drying compounds from other oils containing drying components. For example, by removing about 12% of such saturated compounds from linseed oil, its degree of unsaturation or iodine value was increased from 180 to an equivalent of 212; by removing about 16% from Perilla oil its iodine value was increased from 194 to an equivalent of 234; by removing about 35% from cottonseed oil its iodine value was increased from 110 to an equivalent of 165. Such oils after such treatment have an enhanced value as vehicles for paints, varnishes and similar compositions.

It has been found that this improvement of drying and semi-drying oils is most satisfactorily obtained by first bodying them in a continuous process, at a relatively high temperature and low pressure.

In apparatus and method for the continuous bodying of drying or semi-drying oils heretofore disclosed, a flowing stream of the oil is heated and subjected to a selected heat bodying temperature for a selected period of time while moving slowly through a heated zone of reaction to effect a desired change in the oil, after which the oil is cooled to terminate the reaction.

A serious difficulty has been experienced with such method due to the fact that the oil being treated is not uniform in structure. The oil in passing slowly through the heated reactor becomes progressively more viscous in passing from its inlet to its outlet as it is polymerized and condensed.

A substantial part of the relatively fluid oil supplied the inlet of the reactor will then tend to channel or pass through the mass of more viscous oil, with the result that the oil discharged from the reactor consists of a mixture or blend of the treated oil, some of which has been subjected to the bodying reaction for the full or an excessive period of time and bodied to too great an extent, and some of which has passed through the reactor too quickly and is insufficiently bodied.

Heavily bodied oils so produced usually contain undesirable clots or lumps of gels of the over-treated oil mixed or dispersed in the under-treated more fluid oil.

Moreover, with such a process the decomposition compounds resulting from the bodying reaction are cooled with and remain in the treated oil. Among these decomposition products are fatty acids which often may amount to fifteen per cent. or more by weight of the oil. There is likewise formed considerable amounts of acrolein, aldehydes, ketones, and other derivative compounds of the glycerol and fatty acids, which if they remain in the treated oil adversely affect its value.

The high acid content is objectionable when the oil is to be used as a grinding vehicle for paints and other coatings, since the fatty acids are relatively nondrying and also tend to combine with certain metallic and other pigments to form objectionable slimes and soaps.

Many of the decomposition compounds also tend to impart an objectionable odor and to discolor the product and also act as catalysts in promoting rapid deterioration, disadvantageously affecting the keeping qualities and the color stability of the oil.

It is, therefore, among the further objects of the present invention to provide an improved process of and apparatus for continuously bodying drying or semi-drying oils, which will assure uniform treatment of the oil in passing through the apparatus and in being treated in the process without substantial overtreating of part of the oil or undertreating of other portions of the oil due to non-uniformity of flow caused by increased resistance to flow of the oil as it becomes more viscous in passing from the inlet to the outlet of the reactor.

Still further objects and advantages will appear in the more detailed description set forth below, it being understood, however, that this more detailed description is given by way of illustration and explanation only and not by way of limitation, since various changes therein may be made by those skilled in the art without

departing from the scope and spirit of the present invention.

These objects may be attained by passing the oils continuously through a suitable reactor, in which a confined uniformly flowing stream of the oil is quickly heated with vigorous agitation to a suitable reacting, i. e. polymerizing, temperature, at which temperature the uniformly flowing stream of agitated oil is maintained a sufficient period of time to obtain a desired change in structure and molecular weight resulting from the heat polymerization and condensation of the unsaturated components therein.

The oils may also be heated to the selected bodying reaction temperature before introduction into the reactor, and if desired at least in part by heat exchange with the hot treated oil leaving the reactor.

As the stream flows slowly through the reactor, steam, superheated to a temperature approximately within the polymerizing range of about 540° F. to 700° F., may be introduced into the continuously flowing stream of bodied oil selectively to hydrolyze the contaminating low molecular weight saturated glycerides in the oil to their readily volatilizable fatty acids.

The amount of steam so supplied is correlated to the reduced pressure, the reaction temperature and to the volatility of the contaminates in the heated oil, the amount being sufficient to effect substantial hydrolization and vaporization of such undesired saturated non-drying compounds, without substantial hydrolyzing or vaporization of the valuable higher molecular weight polymers of the unsaturated quick drying compounds.

Finally the steam and volatilized fatty acids and other volatilized non-drying contaminates are removed from the reactor, which preferably is maintained at a relatively high vacuum.

I have found that maintaining the oil in a state of vigorous agitation during the bodying reaction not only assures uniform heat distribution for the reacting, or polymerizing, treatment to the flowing column of oil and the avoidance of by-passing or localized overtreatment, but also substantially accelerates the speed of and the extent of the condensation reaction, in some instances more than doubling the reaction rate, thereby substantially reducing the time required for the treatment.

The agitating action also substantially improves the structure of the highly bodied oil with enhancement of its smoothness and uniformity and results in the substantial absence of objectionable clots or gels.

I have also found it desirable when treating certain oils, to maintain them under a non-oxidizing atmosphere and the influence of a reduced pressure, for instance 5 mm. or less, during the reaction, which not only accelerates the reaction rate, but also facilitates the prompt removal by vaporization substantially as formed of the relatively low boiling volatile poor drying contaminates resulting from the reaction, which may injuriously affect the quality of the oil if allowed to remain therein.

Moreover, treating the oil in an inert or non-oxidizing atmosphere substantially prevents the formation of oxidation compounds which may result in film softness, discoloration and lessen the value of the oil for its intended purpose.

When treating certain oils, for instance castor and other oils containing hydroxyl groups which split or reform during the heating reaction with elimination of water, it may be desirable to subject the oil during the reaction to a relatively high pressure, for instance 2,000 pounds or more, which I have found effects a substantial improvement in the quality and yield of the drying oil product.

It is also advantageous when treating certain drying or semi-drying oils, to mix them with solvent or an oil polymer disperse medium that may have a vaporizing point at atmospheric or the reduced pressure of the reaction below that of the desired reacting temperature, in which event the oil during the heat reaction is maintained at a sufficiently high pressure to substantially prevent such vaporization of the relatively more volatile ingredients.

I have found that reacting the oil under a relatively high reacting pressure results in the production of a somewhat different type of bodying reaction than is effected under substantially lower pressures, and an oil structure having desirable characteristics for many industrial purposes, and which may advantageously be used for blending with the type of drying oils produced under high vacuum conditions.

The accompanying drawings show some of the various forms of the present invention, but to which the invention is by no means restricted, since many changes and alterations may be made therein, all within the scope of the present invention.

Fig. 1 is an elevation diagrammatically illustrating a preferred arrangement of apparatus for continuously preheating the incoming oil before introduction into the bodying reactor and then heat bodying and desaturating drying and semi-drying oils under a reduced pressure with or without the subsequent combination of the hot viscous oil discharged from the reactor with a selected solvent or dispersing medium;

Fig. 2 is an elevation diagrammatically illustrating an alternative arrangement of apparatus for continuously heat treating drying oils under a high pressure, followed by removal of the volatiles by steam at a reduced pressure;

Fig. 3 is an elevation diagrammatically illustrating an alternative arrangement of apparatus for continuously modifying the characteristics of drying oils, in which the heat exchanger and oil preheater is omitted;

Fig. 4 is an elevation diagrammatically illustrating a preferred arrangement of apparatus for continuously bodying and desaturating drying oils, in which the bodied oils are processed to remove undesired non- or slow drying components, by treatment in a multiple plate steam-vacuum still;

Fig. 5 is an elevation diagrammatically illustrating a preferred arrangement of apparatus for continuously bodying and modifying the drying characteristics of oils containing hydroxyl groups, such as castor oil, according to which the oils are first subjected to a catalytic dehydration before they are heat bodied;

Fig. 6 is a longitudinal sectional view of an alternative reactor construction with an enlarged top;

Figs. 7 and 8 are respectively transverse sectional views taken upon the lines 7—7 and 8—8 of Fig. 6, upon an enlarged scale as compared to Fig. 6.

The preferred arrangement of apparatus illustrated in Fig. 1, comprises an oil feed pump 1, which forces a confined rapidly flowing stream of the oil through the pipes 201 and 204, the valve

145 being closed and the valve 144 being opened, to the vacuum oil deaerator 113 of usual and well known construction. This deaerator is operable substantially to remove dissolved and entrained air and objectionable gases from the flowing stream of oil, which then passes by way of pipe 205 and pump 114 to heat exchanger 2. Alternatively, when the valve 145 is opened and valve 144 is closed, the oil may flow directly through pipes 202 and 203 to the heat exchanger 2.

In the exchanger 2, the oil is preheated by heat exchange with the hot bodied oil after the heat treatment thereof.

In the construction shown, oil heater 3 comprises a series of tubes of relatively small cross sectional area having relatively thin walls of electric and corrosion resisting metal through which an electric heating current is passed generating heat therein and through which the oil flows at a rapid rate and is quickly heated to the desired closely controlled discharge temperature. Such a fluid heating apparatus is disclosed in United States Patent 1,985,280. Alternatively, the oil supplied to reactor 5 may be heated by direct flame or high temperature vapors or any other usual and convenient means.

The heated oil then passes to inlet 4 of oil bodying reactor 5 by the pipe 206. The reactor 5 comprises a cylindrical column of suitable cross sectional area and height operable to retard the rate of flow of the stream of oil and retain same in the reactor for the necessary period of time to effect a desired heat reaction to the oil.

The oil passes from reactor 5 by way of discharge connections 6, 7 or 8. The use of alternative outlet connections 6, 7, or 8 will enable variation in the height of oil in the reactor and thereby the reaction period or the time required at a constant rate of flow for the oil to pass therethrough.

The extent of the bodying of the oil is determined by the degree of heat to which it is subjected, and by the period of time during which it is subjected to such heat. The amount of and the point of application of the steam to the oil, the pressure to which the oil is subjected during the reaction, and the kind and quantity of catalyst or reacting medium incorporated with the oil during the heat treatment will also determine the extent of the reaction.

The reactor 5 is provided with agitating blades 12, connected to rotating shaft 13 which passes through vapor-tight outlet and thrust bearing 14 to electric motor 13'. Stationary vertical blades 15 are provided between the rotating blades 12 to prevent the column of oil passing through the reactor from assuming a rapid rotary movement due to the action of rotating blades 12.

The pitch of the rotating blades 12 are preferably opposed and they are preferably placed at right angles to each other on shaft 13, so that they will vigorously agitate and mix the upwardly flowing stream of oil in the reactor in a substantially horizontal plane, thus preventing channeling or by-passing of the more fluid oil supplied to the base of the reactor through the progressively more viscous upwardly flowing oil, and maintaining the stream of oil flowing therethrough at a substantially uniform cross sectional composition and temperature. The vigorous agitation of the oil substantially accelerates the rate or speed and the uniformity of the bodying reaction.

The reactor 5 is also provided with steam inlet and distributor connections 16, 17, 18 and 19, by means of which steam in selected amounts may be supplied to and intimately mixed with the flowing column of reacting oil. The valves 42, 43 and 44 enable control of the steam supply.

In some instances it may be desirable to supply the steam at connection 19 and subject the oil to the action of the steam during the entire reaction period in reactor 5.

The quantity of steam supplied to the flowing stream of oil preferably is sufficient only to react with and hydrolyze and/or to vaporize the relatively low molecular weight saturated compounds in the oil. These saturated compounds and glycerides are thereby selectively converted into their corresponding fatty acids without substantial change to the desirable relatively high molecular weight unsaturated quick drying compounds. The resulting fatty acids, due to their relatively low boiling point, will vaporize and together with the steam are removed from the oil.

The treated oil, substantially separated from free fatty acids and other volatile contaminates, is selectively discharged from reactor 5 by way of discharge connections 6, 7 or 8 to hot oil receiver 9 and discharge pump 10 with flow regulator 11, and then to the heat exchanger 2, where it is quickly cooled to terminate the heat reaction, as by heat exchange with a cooler portion of the same flowing stream of oil. Any vapors released in the receiver 9 are removed by the pressure equalizing conduit 207. The treated oil then flows by conduit 107 to suitable storage.

Reactor 5 preferably is maintained under a reduced pressure, for instance, of 5 to 20 mm. by conventional steam condensing and vacuum producing apparatus 20. The oil and steam vapors pass by way of vapor outlet 21 to fatty acid condenser 22 and the condensate is collected in receiver 23. The steam substantially stripped of readily condensible volatiles passes to and is condensed in vacuum producing means 20.

Reactor 5 preferably is closed to the atmosphere; thus no oxygen or air will contact the oil while passing therethrough so that the thickening or bodying of the oil will result from heat polymerization and condensation without substantial oxidation.

Where it is desired to modify the characteristics of the oil, for instance its surface tension, its order of unsaturation or conjugation, its wetting capacity or to facilitate grinding with certain pigments or other materials, or to modify its penetration and many other properties, it may be desirable to react the oil during the bodying reaction with determinate amounts of oxygen or atmospheric air, sulphur or chlorine vapors. These or other desired and suitable reactants may be introduced and intimately mixed with the flowing stream of oil by way of inlet and distributor connections 16', 17', 18' or 19', either alone or combined with the steam if desired.

The volatilized relatively pure fatty acids may also be selectively separated from other volatiles or contaminates, such as ketones, aldehydes and easily oxidized fatty compounds formed during the heat reaction and which may injuriously affect the color, odor or keeping qualities of the fatty acids. This is because the condensing temperatures of the fatty acid vapors differ from the condensing temperatures of the vapors from the other volatiles and contaminates which may be present.

This selective condensation may be accomplished by using an additional condenser 22, the

cooling and condensing medium supplied the first condenser 22 being so adjusted that the relatively pure high boiling fatty acid vapors only are condensed in said first condenser, while the lower boiling point volatile contaminates pass together with the steam to the second condenser for condensation and collection.

Alternatively, a fractionating column may be substituted for the water cooled condenser 22, and the various volatiles fractionally or selectively condensed and separately collected.

In the arrangement shown, shell 25 of reactor 5 is constructed of steel plate with nickel, "Iconel," or other appropriate corrosion resisting inner surface. Through a wire coil 28, electrically insulated from but in close proximity to the outer steel surface of shell 25, an alternating electric current is passed, generating heat to a desired extent in shell 25 by induction. Alternatively reactor 5 may be heated by direct oil or gas fire, or high temperature vapors, or any other usual or convenient means.

A thermostatic temperature controller 26, with its sensitive element 27 subjected to the temperature of the oil in the reactor, is provided to maintain the oil at a substantially constant determinate temperature during the bodying treatment. The controller 26 controls the solenoid or relay actuated switch 24 which is located in the electric heating circuit leading to coil 28.

The polymerizing reaction will also generate a substantial amount of heat in the oil, due to its exothermic character, varying with the degree of unsaturation of the oil and also the speed and the extent of the polymerizing reaction. When such oils are heated to a high reacting temperature, even though the external heat is discontinued, the exothermic reaction may continue to raise the temperature of the oil to a degree where undesired decomposition may take place.

Therefore, to cool and absorb the excess heat generated in the oil by the exothermic reaction, the reactor 5 is provided with an air cooling arrangement comprising a blower 34 having a connection 32 into the annular space 30 formed between the reactor shell 25 and outer heat insulating shell 31. This space 30 has an air outlet 33. The blower 34 is driven by an electric motor 35 controlled by the solenoid or relay actuated switch 36 and temperature controller 26.

The controller 26 will first operate to supply heating current to coil 28 to raise the oil in the reactor to the predetermined temperature. At this point controller 26 will disconnect the current supply by opening switch 24.

If the temperature of the oil in the reactor continues to rise a predetermined amount, for instance 5 degrees, due to the exothermic reaction or any other cause, the controller 26 will then cause closure of the switch 36 to operate the blower 34 and cause a cooling current of air to flow through annular space 30 in direct contact with the outer surface of reactor shell 25. This will quickly absorb the excess heat and reduce the temperature of the oil in the reactor, thus automatically maintaining the flowing stream of oil in the reactor at a substantially constant predetermined reaction temperature.

Although any drying or semi-drying oil, either alone or combined with other oils or materials, capable of bodying when subjected to the influence of a suitable reacting temperature, may be bodied and its drying characteristics substantially improved by treatment in the apparatus and the manner disclosed herein, the operation will be described by way of illustrative example as applied to a sardine fish oil of commercial quality, which had been previously treated to remove gums, mucilage and other colloidal and suspended impurities from the oil.

The oil is forced into the reactor 5 by pump 1 at a rate, for example, of 2,000 pounds per hour. In the heat exchanger 2, the oil is heated from an initial temperature of 75° to a discharge temperature of 490° F. by exchange with a hotter portion of the same flowing stream, passing then to electric oil heater 3, where it is quickly heated to the desired reaction temperature, for example, 625° F.

This temperature at the outlet of the heater 3 is automatically maintained by the thermostatic controller 37 with its sensitive element 38 positioned on the line 206. Controller 37 will control the voltage regulator 39 to vary the electric current input to the heater to maintain the stream of oil discharged from the heater at a substantially constant determined temperature.

Although the reactor may vary widely in diameter and height, a suitable reactor 5 may be 18 inches in diameter and 22 feet in height.

The heat supplied to the shell 25 of reactor 5 by the heater coil 28 will be sufficient to maintain the oil therein at a desired reacting temperature within the range of polymerizing and hydrolyzing temperatures, for example 625° F.

Since the initial or polymerizing reaction when treating such an oil is quite energetic, a large amount of exothermic heat is generated, principally during the first ten minutes of the reaction, or during the first three or four feet of oil travel through the reactor.

A separate induction heating coil 29 may be provided at the lower portion of reactor 5 to enable readier control. The coil 29 is preferably provided with an independent regulator 41 by which the electric heat input to the lower portion of shell 25 may be separately adjusted. After the initial polymerization, the amount of exothermic heat generated in the oil is relatively small.

Alternatively, electric heating coils 28 and 29 may be constructed with as many sections as desired, so that the heat supplied selected portions of reactor shell 25 may be adjusted in accordance with and correlated to the amount of heat of the exothermic reaction at these points, thus maintaining a substantially uniform temperature gradient over the heated portion of reactor shell 25.

The column of oil flowing slowly upwardly in reactor 5, preferably is subjected to a vigorous agitating and mixing action by the agitator blades 12 rotating at a speed, for example of 150 R. P. M. These will agitate the oil in a substantially horizontal plane and prevent vertical channeling or non-uniform flow of the oil through the reactor, so that the column of oil is uniformly heated throughout its body. The reactor is maintained under a reduced pressure, for example ten millimeters or less, by the vacuum producing apparatus 20.

As the oil progresses through the reactor, the viscosity and molecular weight of its unsaturates gradually increase. The saturated glycerides, however, are not appreciably affected and remain in their original fluid condition. When these saturated relatively non-bodying compounds, which may equal 25% or more of the total weight of the oil being treated, are hydrolyzed by reaction with the steam and removed from the oil by steam vacuum distillation, there

is a sharp increase in viscosity and molecular weight of the drying oil product, and an increase in the speed or rate of the bodying reaction.

To maintain the reacting oil in a relatively fluid condition, it is, therefore, desirable to retain these relatively inert diluting compounds in the solution until the bodying reaction is substantially completed and this will be accomplished by the reactor 5 of Fig. 1.

Distilling steam at a rate for instance of fifteen pounds per hour is supplied and intimately mixed with the flowing stream of oil at the steam inlet 19. The volatiles and decomposition products resulting from the bodying reaction together with the steam, pass from the reactor by the vapor outlet 21.

Hydrolyzing steam at a rate for example of 300 pounds per hour and at a temperature within the hydrolyzing range such as 625° F., preferably is supplied to and intimately mixed with the upper portion of the upwardly flowing body of oil by the steam inlet and distributor 16.

The saturated low molecular weight fatty acids resulting from the hydrolyzing reaction with the steam together with the volatile contaminates will pass with the steam through vapor outlet 21 to water cooled condenser 22 where the fatty vapors are condensed and collected in receiver 23, the steam substantially stripped of fatty material passing together with any non-condensible gases present to condensing and vacuum apparatus 20.

The treated oil which passes by way of outlet 6 to hot oil receiver 9 will be at a temperature of about 625° F. The receiver 9 with pressure equalizing conduit 207 also acts as a vacuum seal. The oil is then forced by discharge pump 10 and flow regulator 11 through heat exchanger 2 where it is quickly cooled to terminate the reaction, for example to 200° F., by exchange with the cool untreated oil.

The following tabulation shows the effect of the above described treatment upon the sardine oil.

	Original oil	Treated oil	Distillate
Weight, per cent	100	76	24
Iodine value	182	108	58
Acid value	3.6	0.3	196
Saponification value	194	247	201
Molecular weight	860	1,920	288
Viscosity, poises	4	320	

The fatty acid distillate consists principally of myristic and palmitic acids, with a small amount of oleic acid and higher unsaturated compounds and is of excellent color and odor.

The bodied drying oil is practically odorless and nearly water white in color and will dry to a hard dry non-tacky film in three hours. This film was not affected by thirty minutes' hot water submersion, and on standing and chilling will not cloud or precipitate solids.

Using a weighted value for the iodine value of the distillate, the equivalent increase in unsaturation of the drying oil due to the removal of the saturated compounds would be equal to an original iodine value of about 232.

The oil may be treated to have any desired viscosity by varying the temperature and the time of the reaction. For example, if the sardine oil is treated at a temperature of 610° F. for 40 minutes, instead of at 625° for 60 minutes, a treated oil will be produced having a viscosity of about 125 poises instead of 320 poises.

The same procedure as above detailed may be used to body the oil only, with the steam hydrolyzing reaction being omitted. Bodying the oil under vacuum, such as the vacuum of 10 mm. of mercury given above with the continuous removal of fatty acids and volatile decomposition products resulting from the bodying reaction, produces a substantially neutral polymerized oil with improved drying characteristics.

Alternatively, when bodying and treating certain oils, either alone or combined with other materials, it may be advantageous to subject the oil while undergoing the bodying reaction to a relatively high pressure instead of a vacuum. An arrangement for this purpose is diagrammatically illustrated in Fig. 2.

In Fig. 2, high pressure oil bodying reactor 45 is provided, constructed of suitable material to resist the high pressure and temperature and the corrosive action of the oil, with agitating mechanism, heating and cooling means and control devices substantially as shown and described in connection with Fig. 1.

The oil to be treated, which preferably has been treated in deaerator 113 to substantially remove moisture, and entrained and dissolved air and gases which may injuriously affect the properties of the oil, is supplied by feed pump 51, of hydraulic or other suitable type at the desired high pressure.

The oil passes through heat exchanger 52 and then through oil heater 53 where it is quickly raised to a determinate reacting temperature. It then passes to inlet 46 at the base of reactor 45. Reactor 45 is so proportioned that a determinate period of time is required for the flowing stream of oil to pass therethrough, for instance 60 to 90 minutes to effect the desired bodying reaction.

The vaporizing and hydrolyzing reactor 55 is provided with the oil outlet 56, the oil inlet 54 and the vapor outlet 58.

The reactor 55 is also provided with electric heating means 62 with an automatic temperature control 63 to maintain the oil passing through the reactor 55 at a substantially constant temperature to effect hydrolyzation of the saturated glycerides to fatty acids, and the vaporization and removal of the fatty acids and other volatile contaminates in the oil, substantially as described in Fig. 1.

The reactor 55 is so proportioned that for example 10 to 20 minutes may be required for the flowing stream of oil to pass from the inlet 54 to the outlet 56. The reactor 55 is preferably maintained under a reduced pressure, for instance 5 mm. or less by the vacuum producing means 20.

Hydrolyzing and vaporizing steam is supplied by the steam inlet 57 and flow regulator 64. The volatilized fatty acids pass together with the steam and with other volatile contaminates by the connection 58 to condenser 22 where the fatty acid vapors are condensed and collected in receiver 23, the steam and any remaining vapors passing to vacuum creating means 20.

The oil substantially stripped of its fatty acids, volatile contaminates and saturated non-drying compounds, passes from reactor 55 by way of the outlet 56 to the receiver 59. The discharge pump 60 then forces it through the heat exchanger 52, where it is quickly cooled to terminate the heat reaction, and then passes to suitable storage.

Alternatively, when the oils are treated to have a relatively low viscosity, the oil discharge receiver 59 and pump 60 may be omitted and the

oil discharged to a suitable vacuum receiver by gravity.

The heat exchanger-oil preheater 52 may also be omitted and the oil heated to the desired reacting temperature during its passage through oil heater 53 and the hot treated oil may be cooled by other usual cooling means.

In some instances it is desirable to effect hydrolysis of the saturated glycerides under a high pressure. For such treatment, high pressure steam is supplied the reactor 45 by way of the steam inlet 49 and steam flow regulator 50, where due to the high pressure and lower oil temperature it is condensed and intimately mixed with the flowing stream of oil, preferably after the substantial completion of the condensation bodying reaction.

Due to the high solubility of the water vapor or water in the oil at high pressure, for example 2,000 pounds per square inch or more, the hydrolyzing reaction will take place very energetically and any unpolymerized or low molecular weight glycerides in the oil will be quickly converted to their fatty acids. The flowing stream then passes by way of pressure maintaining valve 43 to inlet 54 of vaporizing reactor 55.

In the vaporizing reactor 55, the pressure treated oil will be subjected to a reduced pressure, for example of 5 or less mm., whereupon part or all of the fatty acids and low boiling contaminating volatile compounds in the oil flash vaporize and pass from the reactor 55 by the vapor outlet 58.

If desired, reactor 55 may be provided with agitating means and also with cooling means, as shown and described in connection with Fig. 1.

Fig. 3 illustrates diagrammatically an alternative arrangement, in which the heat exchanger 2 and oil heater 3 as shown in Fig. 1 is omitted, and the cool or otherwise preheated oil is supplied directly to the inlet 66 of the reactor 65 and heated to the desired reacting temperature while passing upwardly therethrough.

In Fig. 3, the reactor 65 is provided with a preheating section 67 at its lower portion, for example the lower two feet thereof operable to raise the temperature of the stream of oil flowing therethrough to a determinate reacting temperature.

The preheating section 67 is supplied with suitable oil heating means. In the drawings such means comprises an electrical induction heating coil 70 having a thermostatic controller 71.

Agitating means 69 are provided to effect uniform and rapid transfer of heat from heated surface 68 to the stream of oil.

The thermostatic controller 71 with its heat sensitive element 72 is subjected to the maximum temperature of the oil in the preheating section 67.

The electrically controlled switch 73 is controlled by the controller 71 to regulate the supply of electric heating current to coil 70 to maintain the flowing stream of oil at a substantially constant reacting temperature. The heated oil then passes upwardly through reactor 65, which preferably is maintained at a reduced pressure.

The oil while passing slowly through reactor 65, preferably is mixed with steam supplied through steam inlet 74. The steam so supplied preferably is sufficient only to effect vaporization of the relatively low boiling volatile contaminates which may be produced in the oil by the bodying reaction, without substantial hydrolyzing effect upon the glycerides.

If desired, catalyzing or reacting media commonly used for the purpose may be supplied to and incorporated with the flowing stream of oil in a like manner, to accelerate the bodying reaction or by reacting with the oil to effect a desired isomeric or other change in the composition of the oil.

To effect the substantial removal of saturated and non-drying glycerides in the oil, an additional quantity of steam is supplied to the flowing stream of oil, preferably by way of the steam inlet 75. The steam so supplied preferably is sufficient at the temperature to which it is superheated to react with and convert the relatively low molecular weight saturated glycerides, or those having less than 18 carbon atoms in the molecule, without substantial change to the higher molecular weight bodied unsaturated glycerides, to their corresponding fatty acids. These fatty acids then vaporize and pass from the oil together with the steam through the outlet 21.

The treated oil passes from reactor 65 by oil outlet 77 through oil cooler 78, where it is cooled to terminate the heat reaction. The oil then passes to vacuum oil receiver 79 from which it is removed by oil discharge pump 80 to storage.

Fig. 4 illustrates an alternative arrangement of apparatus for continuously bodying and purifying drying oils in which the volatile contaminates are relatively more difficult to hydrolyze and distill.

The preferred arrangement shown in Fig. 4 is somewhat similar to that shown and described in Fig. 3, except that alternative means are provided to vaporize and remove the relatively higher boiling contaminates from the flowing stream of oil.

The oil after being bodied to the desired extent in bodying reactor 65 and after the relatively low boiling contaminates, such as certain free fatty acids and decomposition products resulting from the bodying reaction are vaporized and removed by way of the outlet 21, still may contain substantial amounts of relatively higher boiling undesirable non-drying glycerides.

To remove these relatively refractive contaminates, the oil at its hydrolyzing temperature is passed by outlet 77 of the reactor 65 to the inlet 94 of vaporizer or still 90. The vessel 90 preferably has a plurality for instance 5, of superimposed distilling plates 91, which if desired may be independently heated to a desired distilling and hydrolyzing reacting temperature by electrical or other suitable or convenient means. The plates 91 are fitted with bubble caps 92 and overflow down pipes 93. Vaporizing vessel 90 preferably is maintained at a low vaporizing pressure, for example 3 to 5 mm. or less.

The oil containing the relatively high boiling contaminates passes downwardly over the plates 91 and steam, preferably superheated to hydrolyzing temperature, is supplied by the steam inlet 97 to the base of still 90. This steam will pass upwardly through distilling plates 91 by the slots in the skirts of bubble caps 92 counter current to the descending oil.

The steam mixes intimately with the heated oil, hydrolyzing and/or vaporizing and removing the residual less readily volatile relatively low molecular weight saturated non-drying glycerides, and other contaminates from the oil. The volatile contaminates consisting principally of saturated glycerides and fatty acids, together with the steam pass by vapor outlet 96 to con-

denser 98 and there they are condensed and collected in receiver 99. The steam substantially stripped of fatty vapors passes by outlet 101 to the vacuum producing means 20.

The purified oil substantially freed from non-drying and other non-desirable contaminates, flows from the still 90 by the outlet 95 to the cooler 78 where it is quickly cooled to a non-reacting temperature and it then flows to receiver 79 from which it is forced by pump 80 to storage.

The heat bodying reaction results in a gradual increase in viscosity with the unsaturated polymers being soluble, or dispersible, in the relatively unchanged or saturated portion of the oil until a saturation point is reached, when they will quickly gel or solidify. This condition is more pronounced when the oil is first bodied to a high viscosity in the reactor 65 and the relatively inert or disperse phase is then removed by distillation in the vaporizer 90 of Fig. 4.

Alternatively, the oil may be treated to have a very high degree of polymerization and nevertheless maintained in a suitable fluid condition if a suitable amount of a fluidizing medium, for example an amount equal to or less than the amount of the non-drying disperse phase or non-drying contaminates to be removed by distillation, is incorporated with the oil prior to the final polymerization.

Preferably, resin, ester gum or other similar oil soluble or dispersible material, having a suitable low viscosity when hot, and a high vaporizing temperature together with the ability to form a hard dry film when combined with the oil upon cooling, may be utilized as the dispersing medium to maintain the oil polymer at the desired state of fluidity during the bodying and hydrolyzing reactions.

These fluidizing or dispersing materials may be incorporated with the flowing stream of oil prior to the heat reaction, or before or during the removal by distillation of the saturated relatively non-drying contaminates from the oil.

In many instances, particularly when the oil is bodied to relatively high viscosity, for instance 2000 poises or more at 77° F. and/or when resins or other materials have been incorporated with the oil before or during the bodying reaction, it may be desirable to dilute or thin the highly viscous oil by incorporating therewith a volatile solvent which is miscible with the oil or oil-resin blend, thereby reducing the viscosity of the material, for example to 10 to 20 poises at 77° F., to facilitate its use in subsequent operations, such as brushing or spraying in a thin film as a varnish, grinding with pigments, and many other uses.

I have found that by polymerizing and condensively reacting the unsaturated oil and certain resins at relatively high temperatures, for instance at 610 to 640° F. or more for a selected period of time, for instance 30 to 60 minutes, while subjected to vigorous agitation and a reduced pressure, the oil and resins react energetically and combine to form desirable high molecular weight compounds and that under the above high temperature conditions the reactions are more complete and effective than when the oils and resins are combined at lower temperatures, for instance 560 to 585 F. as in usual open kettle varnish compounding practice.

I have also found that when such a reacted or highly bodied compound is reduced in viscosity or thinned by dispersion in a suitable solvent material, for instance highly volatile petroleum or coal tar derivatives, in which it is soluble, at a high temperature, for instance 600 to 640° F., the dispersion of the oil resin compound in the solvent is more complete and uniform and imparts a degree of uniformity and smoothness to the varnish or coating film not possible when the compound is thinned at the usual low temperatures of 300 to 450° F. as in usual open kettle practice necessary on account of the low flash point of the volatile solvents and the danger of fire or explosion.

While any suitable and usual means may be utilized to disperse or mix the bodied oil compound and the solvent material, a preferred arrangement of apparatus is illustrated in Fig. 1.

In the preferred arrangement, a determinate quantity of a selected volatile solvent material, such as petroleum or coal tar derivatives, turpentine or other suitable solvent in which the oil is substantially soluble or dispersible, is continuously supplied by means of solvent feed pump 105, to mixing device 106 of common and usual construction, through which the flowing stream of oil-resin compound is flowing at a relative high temperature, for instance 625° F. and at a high viscosity, for instance 2000 poises at 77° F., and in which the oil compound is effectively dispersed and/or substantially dissolved in the solvent material, the mixture of oil compound and solvent reduced to a desired low viscosity, for instance 10 poises at 77° F., passing then to cooler and heat exchanger 2 where its temperature is reduced to a substantially non-reacting temperature, for instance 175° F., and finally passing to suitable storage facilities.

In the above described preferred methods of operation, crude or substantially unbodied oil was used as the charging stock. Alternatively, the charged oil may be bodied wholly or in part prior to being subjected to the desaturating treatment, the oil to be treated to improve its drying characteristics being treated in the manner described and its molecular weight increased to the desired extent, after which it is subjected to the aforesaid desaturating treatment to effect substantial removal of the non-drying saturated contaminates, in the manner heretofore described.

Certain oils, for example castor oil, containing hydroxyl groups, in their natural state have relatively inferior drying and film-forming characteristics. The drying properties of such an oil may be greatly improved however by first subjecting it in a continuous manner to a dehydrating and then subsequently to a heat bodying reaction.

While the hydroxyl groups may be removed and the oil modified to the ethylenic type with substantial increase in unsaturation and drying ability by a continuous heat treatment alone, a relative long exposure of the oil to high reacting temperature is required and unless extreme care is exercised, such treatment may result in deterioration of the drying properties of the oil.

It has been found that this may be overcome by accelerating the dehydration by suitable catalysts or activators.

Among suitable catalysts commonly used for the purpose are non-oxidizing acids, such as sulfuric, hydrochloric or acetic acids, strong alkalies or heavy metal salts, the oxides of aluminum, zinc and many other metals and other similarly acting organic and inorganic compounds.

The catalyst preferably is combined with a

suitable porous bulking or distributing medium, such as fuller's or diatomaceous earth, which is first impregnated with the catalyst and then mixed with the oil.

The catalyst may be mixed with the flowing stream of oil, either before or during the heating. Preferably the catalyst is supplied as a thin paste or slurry mixed with a small proportion of the oil being treated and then intimately combined with the flowing stream of oil prior to heating.

The flowing stream of mixed oil and catalyst is then quickly heated to a dehydrating reaction temperature, usually within the range of 450 to 550° F. and maintained in a state of vigorous agitation a determinate period of time, for example, one to three minutes, to effect the desired dehydration reaction.

In some instances, the dehydrating reaction may be performed under a high pressure, for example 750 to 1000 pounds gauge or more.

The flowing stream of dehydrated oil is preferably then subjected to a reduced pressure, whereupon the water and other volatile contaminates resulting from the dehydrating reaction vaporize and are removed from the oil. The oil then passes to a clarifier means where the catalyst and its carrier and other solid contaminates present are removed.

The dehydrated oil with its degree of unsaturation increased, for example from an initial iodine value of 88, to 143 and with a substantial decrease in viscosity, for example from an initial viscosity of 7.2 to 4.7 poises at 77° F., is then subjected to a polymerizing and condensation reaction at a relatively high temperature, for example within the range of 575 to 625° F., for a determinate period of time, for example for 30 to 50 minutes or more, to effect the desired increase in viscosity and improved film and drying characteristics.

During the bodying reaction, the flowing stream of oil is preferably subjected to vigorous agitation and to a reduced pressure and is steam distilled to remove fatty acids and other volatile relatively nondrying contaminates therefrom. Then the flowing stream of purified oil, converted by the aforesaid treatment from a product having inferior drying properties, to one having very desirable quick drying and film-forming characteristics, is quickly cooled to terminate the heat reaction.

The arrangement illustrated in Fig. 5 is particularly adapted for continuously dehydrating and bodying such oils together with a deaeration step and a catalyst addition step.

In Fig. 5 the oil is supplied, for example at a rate of 1000 pounds per hour, by oil feed pump 110 to a mixing device 111. Supply pump 112 is operable to continuously supply a determinate amount of a selected catalyst, for example about 25 pounds per hour of finely divided fuller's earth impregnated with about one half pound or more of concentrated sulphuric or other suitable non-oxidizing acid in the form of a thin paste or slurry with a small amount of the same oil as under treatment, which is intimately mixed with the flowing stream of oil in mixing device 111.

In the deaerating tank 113 of known and usual construction, a reduced pressure is applied, for example of 20 mm. or less, and any dissolved or entrained air or objectionable gases or volatile material is substantially removed from the oil. The oil then passes through the pump 114 to heat exchanger 115. In the exchanger 115, the hot treated oil temperature is elevated for example from an inlet temperature of 80° to a discharge temperature of 540° by exchange with the hot treated oil.

The oil then passes to oil heater 116 where it is quickly raised to a dehydrating reaction temperature, for example of 490° F. Then the oil passes to the dehydrating reactor 117.

The flowing stream of oil and catalyst is vigorously agitated in the dehydrator reactor 117. The dehydrator 117 may be of any suitable construction. In the preferred arrangement it comprises a coil of tubing or pipe constructed of suitable corrosive resisting metal, operable to retain the flowing stream in a state of vigorous agitation and turbulence for a determinate period of time, for example two minutes or more, during which time the dehydration reaction is substantially completed. The oil while passing through dehydrator 117 is preferably maintained at a selected reacting pressure, for example 425 lbs. gauge by the pressure maintaining valve 118.

The stream of dehydrated oil and eliminated water resulting from the reaction then passes to inlet 119 of vaporizing vessel 120, which is preferably in the form of a cylindrical shell 121 with a concentric interior tubular member 122 spaced from the bottom of vessel 120 and extending upwardly in a vapor-tight manner through the top of vessel 120 to the vapor outlet 123.

The outer shell 121 is provided with inlet 119, arranged to introduce the oil and vapors thereto in a horizontal tangential manner, causing the mixture of oil and water and other vapors to whirl downwardly in a circumferential manner at a rapid rate in the annular space 124 formed between members 121 and 122. The volatile contaminates are vaporized and pass by way of outlet 123 to the vacuum producing means 20, the oil and catalyst separated from the vapors by centrifugal force, deposit on and flow down the side of and collect in the base of vaporizing vessel 120.

The dehydrated oil and catalyst, substantially stripped of volatile contaminates, pass by oil connection 125 and pump 126 to clarifier 127, which may be a filter or centrifuge, preferably of the continuous type, in which the catalyst and its carrier is substantially removed.

The purified dehydrated oil substantially freed of water and catalyst, with its iodine value increased, for example from an initial value of 88, to 142 and its viscosity reduced from an initial value of 7.2 poises, to 4.6 poises at 77° F., passes by way of oil pump 128 to oil heater 129 where its temperature is quickly raised to a determinate bodying reaction temperature, for example of 610° F. It then passes to inlet 130 of the bodying reactor 131.

The flowing stream of oil passes upwardly through reactor 131, where it is subjected to vigorous agitation and maintained at the bodying temperature, for example 610° for a determinate period of time, for instance 40 minutes or more at a selected reduced pressure, for instance 10 mm., in substantially the same manner as described in Fig. 1.

Steam, preferably superheated, is supplied for example at the rate of 150 lbs. per hour, to the flowing stream of oil by the steam inlet 132 and vaporizes and substantially removes fatty acids and other volatile contaminates resulting from the bodying reaction. These volatiles pass to-

gether with the steam to the condensing and vacuum producing means 22 and 20.

The flowing stream of dehydrated bodied oil passes from reactor 131 by oil outlet 134. The treated oil then will have been converted to a product having desirable quick drying and film-forming qualities, with a viscosity for example of 50 poises at 77° F. and an acid value of 1.5. The treated oil is forced by discharge pump 135 through heat exchanger 115 where it is cooled to a non-reacting temperature, for example 100° F., by exchange with a cooler portion of the same flowing stream, passing by the conduit 148 to storage, not shown.

Alternatively, when using a catalyst that may be allowed to remain in the oil, for example a catalyst in a vapor form, or an acid compound of the same oil, that is under treatment, for example, a chlorinated or sulphonated castor oil, or a relatively non-reacting metallic oxide or salt of said acids, preferably one that is substantially soluble in the oil, after completion of the dehydrating reaction in reactor 117, if desired the oil may be passed directly by way of valved connections 136 and 137 and the conduit 138 to the inlet 130 of the bodying reactor 131 in which the water liberated by the dehydration reaction, usually amounting to 5 to 8% by weight of the oil treated, is removed and the oil bodied in one operation.

Such an arrangement avoids the use of vaporizing chamber 120, clarifier 127 and the reheater 129, the relatively small amount of catalyst or activating material, usually amounting to less than 0.005% by weight of the oil, remaining in solution or suspension in the finished product, will not be objectionable for many uses.

In Figs. 6 to 8 is shown an assembly which may be utilized in connection with the reactors of Figs. 1 to 5 to provide the agitating arrangement and also the necessary bearings for the central shaft 13 along the height of the reactors.

In Fig. 6 the shaft 13 passes through bearings 300, 301, 302, 303 and 304. The bearing 307, is best shown in cross section on Fig. 7, upon a somewhat enlarged scale, is mounted upon the plate 15 by the bolts 305, which hold the two bearing elements 306 and 307 together and clamp them against the central portion of the plate 15.

The various plates 15, which are positioned at spaced intervals along the inner shell 308 of the reactor, are attached by the flanges 309 to the vertical bars 310, which extend the full length of the reactor.

Positioned between the bars 310 are the bars 311, which are connected to the bars 310 by the circular strips 312, which are attached to said bars 310 and 311 at spaced intervals.

Between the bearings 301, 302 and 303 and between the baffles or plates 15 are positioned the inclined agitating vanes or plates 12 and at the bottom of the shell 308 there is provided a series of agitators 313 which are vertical and which serve to create a substantial agitation or rotary motion in the lower or preheating portion of the reactor.

In the construction shown in Fig. 6, it has been found desirable to enlarge the upper portion of the shell 308, as indicated at 314 and 315, to provide an increased space for the separation and escape of vapors or volatilized fatty acids or other contaminates removed from the upwardly flowing stream of the oil being bodied.

As shown in Figs. 6 to 8, it is possible first to assemble the structure carrying the fixed plates 15 and the agitating vanes 12 and 313 and then insert the entire structure inside of a tower or other suitable form of reactor shell, as indicated at 308—314—315 in Fig. 6 or 25 in Fig. 1.

While the invention has been described particularly with reference to the treatment of certain oils, it is obvious that its use may be extended to the bodying of any drying or semi-drying oil of the unsaturated ester type or of mixtures of such oils, and to the desaturation of any such oil containing saturated contaminates, and that the drying and other desirable characteristics of such oils may be substantially improved and their value enhanced by the treatment disclosed herein.

It will also be obvious that many other embodiments of the invention may be made by those skilled in the art and it will be therefore understood that the particular devices and arrangement of apparatus and methods of operation shown and described herein are of an illustrative character and are not restrictive, and that various changes in form, construction or arrangement of parts and methods of use may be made within the spirit and scope of the invention as set forth in the following claims.

I claim:

1. The method of continuously treating, glyceride drying and semi-drying oils, to improve their drying characteristics which comprises subjecting a confined stream of the oil flowing upwardly in a reactor column to a bodying temperature for a period of time correlated to the said bodying temperature adequate to effect substantial increase in the molecular weight of the oil, agitating said stream of oil to maintain the same substantially uniform in cross-sectional composition, and continuously removing volatile contaminates as the said bodying reaction proceeds.

2. The method of continuously treating, glyceride drying and semi-drying oils, to improve their drying characteristics which comprises subjecting a confined upwardly flowing stream of the oil to the influence of a bodying temperature for a period of time correlated to said bodying temperature adequate to effect substantial increase in the molecular weight of the unsaturated components of the oil, agitating said stream of oil to maintain the same substantially uniform in cross-sectional composition, continuously subjecting said stream as it is so reacted to distillation continuously to vaporize and remove low molecular weight relatively volatile contaminates from the high molecular weight products of the unsaturate components, and separately cooling the liquid and vapor products of the reaction.

3. The method of continuously treating, glyceride drying and semi-drying oils, to improve their drying characteristics which comprises subjecting a confined stream of the oil flowing upwardly in a reactor column to a bodying temperature for a period of time correlated to the said bodying temperature adequate to effect substantial increase in the molecular weight of the unsaturated components of the oil, continuously subjecting the said stream as it is so reacted to distillation continuously to vaporize and remove low molecular weight relatively volatile contaminates from the high molecular weight products of the unsaturate components, and by mixing the oil of the upwardly flowing stream across the path of its flow maintaining the said stream substantially uniform in cross-sectional composition.

4. The method of continuously treating, glyceride drying and semi-drying oils containing non-

drying contaminates which comprises subjecting a confined stream of the oil flowing upwardly in a reactor column to a bodying temperature for a period of time correlated to said bodying temperature adequate to effect by polymerization substantial increase in the molecular weight of the unsaturated components of the oil, subjecting the said stream of oil as the bodying reaction proceeds to distillation continuously to vaporize and remove low molecular weight relatively volatile contaminates, continuously subjecting the bodied portion of the said stream of oil flowing in the reactor column to the influence of steam in a quantity and at a temperature to effect in the bodied portion of the stream hydrolysis of unbodied components into relatively volatile contaminates and to vaporize and remove said relatively volatile contaminates continuously from the said stream as they are formed therein, and by mixing the oil of the upwardly flowing stream across the path of its flow maintaining the said stream substantially uniform in cross-sectional composition.

5. The method of continuously treating, glyceride drying and semi-drying oils containing non-drying contaminates which comprises subjecting a confined stream of the oil flowing upwardly in a reactor column to a bodying temperature for a period of time correlated to said bodying temperature adequate to effect by polymerization substantial increase in the molecular weight of the unsaturated components of the oil, subjecting the said stream of oil as the bodying reaction proceeds therein to distillation continuously to vaporize and remove low molecular weight relatively volatile contaminates, continuously subjecting the bodied portion of the said stream of oil flowing in the said reactor column to the influence of steam in a quantity and at a temperature to effect in the bodied portion of the stream hydrolysis of unbodied components into relatively volatile contaminates and to vaporize and remove said relatively volatile contaminates continuously from the said stream as they are formed therein, and agitating the said stream of oil during its passage through the reactor column to maintain the same substantially uniform in cross-sectional composition.

6. The method of continuously treating glyceride drying and semi-drying oils containing non-drying contaminates which comprises heating to a polymerizing temperature a confined stream of the oil of substantially uniform cross-sectional composition flowing upwardly in a reactor column combined with an oil-soluble thermoplastic polymer-dispersing resin, reacting the said upwardly flowing stream at said bodying temperature for a period of time correlated to said bodying temperature to effect substantial increase in the molecular weight of the oil by polymerization of the unsaturated components thereof, by subjecting said reacting stream in the reactor column to the influence of reduced pressure and an adequate quantity of steam hydrolyzing, vaporizing, and removing the non-drying contaminates therefrom in the form of relatively volatile decomposition products, and discharging the said stream from the reactor column approximately free of volatile contaminates.

7. The method of continuously treating glyceride drying and semi-drying oils containing non-drying contaminates which comprises heating to a polymerizing temperature a confined stream of the oil of substantially uniform cross-sectional composition flowing upwardly in a reactor column, reacting the said upwardly flowing stream at said bodying temperature for a period of time correlated to said bodying temperature to effect substantial increase in the molecular weight of the oil by polymerization of the unsaturated components thereof, by subjecting said reacting stream in the said reactor column to the influence of reduced pressure and an adequate quantity of steam hydrolyzing, vaporizing, and removing non-drying contaminates therefrom in the form of relatively volatile decomposition products, and discharging the said stream from the reactor column approximately free of volatile contaminates.

8. The method of continuously treating glyceride drying and semi-drying oils which comprises heating to a bodying temperature a confined stream of the oil of substantially uniform cross-sectional composition flowing upwardly in a reactor column, reacting said stream of oil at said bodying temperature for a period of time adequate to effect substantial increase in the viscosity of the oil, continuously freeing the said stream of its relatively volatile contaminates by distillation as the bodying reaction proceeds, substantially reducing the viscosity of the said stream of hot reacted oil by intimately mixing a blending solvent therewith, and discharging the said stream of reacted and thinned oil from the reactor column approximately free of volatile contaminates.

9. The method of continuously treating, glyceride drying and semi-drying oils, to improve their drying characteristics which comprises heating a stream of the oil flowing upwardly in a reactor column to a bodying temperature, reacting said stream at said bodying temperature for a period of time adequate to effect a substantial increase in the viscosity of the oil, continuously freeing the said stream of its relatively volatile contaminates by distillation under reduced pressure as the bodying reaction proceeds, by mixing the oil of the upwardly flowing stream across the path of its flow maintaining the said stream substantially uniform in cross-sectional composition, and discharging the said stream of reacted oil from the reactor column approximately free of volatile contaminates.

10. The method of continuously treating glyceride drying and semi-drying oils to improve their drying characteristics which comprises subjecting a confined stream composed of a mixture of the oil and an oil-soluble thermoplastic polymer-dispersing resin flowing upwardly in a reactor column to a bodying temperature for a period of time correlated to the said bodying temperature adequate to effect a substantial increase in the molecular weight of the oil, agitating said stream of oil to maintain the same substantially uniform in cross-sectional composition, and continuously removing volatile contaminates as the said bodying reaction proceeds.

11. The method of continuously treating glyceride drying and semi-drying oils to improve their drying characteristics which comprises subjecting a confined stream composed of a mixture of the oil and an oil-soluble thermoplastic polymer-dispersing resin flowing upwardly in a reactor column to a bodying temperature for a period of time correlated to the said bodying temperature adequate to effect a substantial increase in the molecular weight of the oil, by mixing the oil of the upwardly flowing stream across the path of its flow maintaining the said stream substantially uniform in cross-sectional composition, and continuously removing volatile

contaminates under reduced pressure as the said bodying reaction proceeds.

12. Apparatus for the continuous treatment of glyceride drying and semi-drying oils comprising a pre-heater organized to heat a confined flowing stream of the oil to a bodying temperature, a reactor column communicating adjacent its lower end with said pre-heater, pressure-creating means organized to force oil through said pre-heater and in an upwardly flowing stream through the said reactor column at a rate related to the bodying temperature of the oil to provide a treating period sufficient to effect by heat-polymerization substantial increase in the molecular weight of the oil, heating and cooling means associated with the said reactor column and arranged to maintain the stream of oil in the said reactor column at a substantially constant bodying temperature, vacuum-creating means associated with the said reactor column and effective on the said stream of oil therein, and agitating mechanism in the said reactor column organized horizontally to agitate the said flowing oil stream therein to maintain said stream of substantially uniform cross-sectional composition.

13. Apparatus for the continuous treatment of glyceride drying and semi-drying oils comprising a pre-heater organized to heat a confined flowing stream of the oil to a bodying temperature, a reactor column communicating adjacent its lower end with said pre-heater, pressure-creating means organized to force oil through said pre-heater and in an upwardly flowing stream through the said reactor column at a rate related to the bodying temperature of the said oil to provide a treating period sufficient to effect by heat-polymerization substantial increase in the molecular weight of the oil, heating and cooling means associated with the said reactor column and arranged to maintain the stream of oil in the said reactor column at a substantially constant bodying temperature, agitating mechanism in the said reactor column organized horizontally to agitate the said flowing oil stream therein to maintain said stream of substantially uniform cross-sectional composition, and steam-supply connections organized to supply vaporizing steam to the reacting upwardly flowing oil stream in the said reactor column.

14. Apparatus for the continuous treatment of glyceride drying and semi-drying oils comprising a pre-heater organized to heat a confined flowing stream of the oil to a bodying temperature, a reactor column communicating adjacent its lower end with said pre-heater, pressure-creating means organized to force oil through said pre-heater and in an upwardly flowing stream through the said reactor column at a rate related to the bodying temperature of the said oil to provide a treating period sufficient to effect by heat-polymerization substantial increase in the molecular weight of the oil, heating and cooling means associated with the said reactor column and arranged to maintain the stream of oil in the said reactor column at a substantially constant bodying temperature, agitating mechanism in the said reactor column organized horizontally to agitate the said flowing oil stream therein to maintain said stream of substantially uniform cross-sectional composition, and steam-supply connections arranged to supply to the oil stream in said reactor column steam in a quantity and at a temperature adequate to hydrolyze and to vaporize the saturated and unpolymerized components of the said oil stream.

15. Apparatus for the continuous treatment of glyceride drying and semi-drying oils comprising a pre-heater organized to heat a confined flowing stream of the oil to a bodying temperature, a reactor column communicating adjacent its lower end with said pre-heater, pressure-creating means organized to force oil through said pre-heater and in an upwardly flowing stream through the said reactor column at a rate related to the bodying temperature of the said oil to provide a treating period sufficient to effect by heat-polymerization substantial increase in the molecular weight of the oil, heating and cooling means associated with the said reactor column and arranged to maintain the said stream of oil in the said reactor column at a substantially constant bodying temperature, agitating mechanism in the said reactor column organized horizontally to agitate the said flowing oil stream therein to maintain said stream of substantially uniform cross-sectional composition, steam-supply connections organized to supply steam to the reacting upwardly flowing oil stream in the said reactor column, and vacuum-creating means associated with the said reactor column and effective on the stream of oil therein.

16. Apparatus for the continuous treatment of glyceride drying and semi-drying oils comprising a reactor column, oil-supply connections adjacent the lower end of said column, means organized to force a stream of oil upwardly through the said reactor column at a controllable rate, heat-supplying and temperature-controlling means associated with the said reactor column and arranged to maintain the stream of oil therein at a bodying temperature, and agitating mechanism in the said reactor column organized horizontally to agitate the said flowing stream therein to maintain the said stream of substantially uniform cross-sectional composition.

17. Apparatus for the continuous treatment of glyceride drying and semi-drying oils comprising a reactor column, oil-supply connections adjacent the lower end of the said column, means organized to force a stream of oil upwardly through the said reactor column at a controllable rate, heat-supplying and temperature-controlling means associated with the said reactor column and arranged to maintain the stream of oil therein at a bodying temperature, agitating mechanism in the said reactor column organized horizontally to agitate the said flowing oil stream therein to maintain the said stream of substantially uniform cross-sectional composition, and steam-supplying connections organized to supply vaporizing steam to the reacting upwardly flowing oil stream in the said reactor column.

18. Apparatus for the continuous treatment of glyceride drying and semi-drying oils comprising a reactor column, oil-supply connections adjacent the lower end of the said column, means organized to force a stream of oil upwardly through the said reactor column at a controllable rate, heat-supplying and temperature-controlling means associated with the said reactor column and arranged to maintain the stream of oil therein at a bodying temperature, agitating mechanism in the said reactor column organized horizontally to agitate the said flowing oil stream therein to maintain the said stream of substantially uniform cross-sectional composition, and vacuum-creating means associated with the said

reactor column and effective on the stream of oil therein.

19. Apparatus for the continuous treatment of glyceride drying and semi-drying oils comprising a reactor column, oil-supply connections adjacent the lower end of the said column, means organized to force a stream of oil upwardly through the said reactor column at a controllable rate, heat-supplying and temperature-controlling means associated with the said reactor column and arranged to maintain the stream of oil therein at a bodying temperature, agitating mechanism in the said reactor column organized horizontally to agitate the said flowing oil stream therein to maintain the said stream of substantially uniform cross-sectional composition, steam-supplying connections organized to supply vaporizing steam to the reacting upwardly flowing stream in the said reactor column, and vacuum-creating means associated with the said reactor column and effective on the stream of oil therein.

20. The method of continuously treating glyceride drying and semi-drying oils containing non-drying contaminating components to improve their drying characteristics, which comprises subjecting a stream of the oil flowing upwardly in a reactor column to a bodying temperature for a period of time correlated to the said bodying temperature adequate to effect by polymerization substantial increase in the molecular weight of the unsaturate components of the oil, and continuously subjecting the said polymerized oil stream to hydrolysis of the unpolymerized non-drying components thereof by introducing into the said oil stream while maintaining it under vacuum and at a temperature higher than 600° F., steam super-heated to a like elevated temperature in large quantity adequate substantially to effect hydrolysis of the said non-drying components, and continuously distilling off from the reactor column decomposition products formed by hydrolysis of the said unpolymerized non-drying components of the oil under the steam and vacuum of the treatment.

21. The method of continuously treating glyceride drying and semi-drying oils containing the polymers of unsaturated components of the oil and unpolymerized non-drying contaminating components to improve their drying characteristics, which comprises subjecting a stream of the said polymerized oil flowing upwardly in a reactor column and maintained under vacuum and at a temperature higher than 600° F. to hydrolysis of the unpolymerized non-drying components thereof by introducing into the said polymerized oil steam super-heated to a like temperature and in large quantity adequate substantially to effect hydrolysis in the oil, and continuously distilling from the reactor column decomposition products formed by hydrolysis of the said unpolymerized non-drying components of the oil under the steam and vacuum of the treatment.

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