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TREATMENT OF CONJUGATED OILS

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This invention broadly relates to a method of altering the normal drying characteristics of conjugated drying oils and conjugated drying oil modified natural and synthetic resin varnishes. Typical conjugated oils are dehydrated castor, and oiticica oil, China-wood or tung oil. Normally, or without auxiliary treatment, such oils and varnishes when applied in thin films and dried, yield optically undesirable surfaces. The light reflected therefrom often is aberrated due to a wrinkling, frosting or gas-checking of the surface of the film and the fault is variously labelled. The defect is herein referred to generally as "surface aberration." Gases which often cause such surface aberration as carbon monoxide, carbon dioxide and methane. The treatment to prevent this condition is sometimes referred to herein as "Gas-proofing." The problem is less serious with some oils (e. g., dehydrated castor) and very serious with others (e. g., China-wood).

The invention relates particularly to auxiliary methods of treating such a conjugated oil, especially China-wood oil, to prevent surface aberration of dried films deposited from coatings containing the said oil.

China-wood or tung oil has many outstanding qualities which make it an invaluable material for use in protecting surfaces and as a general binder for both pigmented and non-pigmented products. It dries rapidly, and has excellent waterproofing quality. However, the defect in the dried film which causes aberration of light incident upon its surface has long been a major obstacle to free use of tung oil.

One theory explains that the defect is due to unequal volume changes within the applied film during and subsequent to a sol-to-gel transformation. The surface of the film may increase in volume due to oxygen fixation and oxygen linkages at the surface. Slow penetration of the oxygen through the depth of the film allows the interior hardening to occur principally by polymerization with little change in volume. Stresses set up between the expanded air-film interface and the interior of the film result in a wrinkling condition, more or less severe, depending in a great part upon the environment of the film during the drying period. The resulting dried films lack the smoothness and gloss expected in coating compositions and such a defect is objectionable in all but a few specialized applications, e. g., wrinkle finishes.

Inasmuch as the surface aberration of dried tung oil films and films resulting from varnishes made with tung oil is a major objection to its

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use there have been a number of methods proposed to accomplish the desired result of glass-smooth films from this valuable drying oil.

An object of the invention is to alter the drying characteristics of a conjugated drying oil, especially tung or China-wood oil, so that after treatment it will form, upon application and drying, a clear, hard film free from surface aberration such as wrinkling, frosting, and gas-checking, which dries without impairment of the normal drying rate, nor is so bodied, or polymerized by the treatment as to be limited in usefulness in specialized protective and decorative coatings.

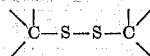
Another object is to produce coating compositions, either clear or pigmented, containing appreciable quantities of tung oil so modified by a catalytic treatment as to provide films free from surface defects normally present when tung oil is employed without proper prior treatment.

Still another object is to produce a tung oil which is not impaired in its speed of drying upon exposure in a film, and which will, upon drying in a gas-contaminated atmosphere, be free from gas-checking.

A specific object is to produce a tung oil vehicle which will be substantially unbodied, not retarding in its speed of drying in a film, and which upon drying alone or in combination with other ingredients will yield a smooth film, free from surface aberration.

Another specific object is to produce a new and useful bodied oil which is derived from a conjugated oil normally subject to surface aberration but which after treatment in accordance with this invention does not have such characteristic. Other objects will appear hereinafter.

The above objectives are accomplished broadly by treating the conjugated drying oil, e. g., tung oil, at elevated temperatures in the presence of minute or catalytic amounts of organic polysulfides containing the group



The compounds of this nature found in petroleum distillates above the mineral spirits fraction, particularly the kerosene fraction, were first found suitable and expedient.

An initial investigation disclosed that if not more than 70% of tung oil and not less than 20% of a volatile hydrocarbon solvent of a distillation range above mineral spirits were refluxed together for from one to four hours within a temperature range of from 425 degrees to 525 degrees F., the temperature being determined by the proportion

and boiling points of the solvent or solvents used in ratio to the percentage of raw tung oil or tung oil and resinous material undergoing the reflux treatment, the resultant oil was materially improved thereby. The preferred temperature range for solvent treatment was found to lie between 450 degrees and 525 degrees F. Suitable petroleum fractions were found to distill between 350 degrees and 500 degrees F., with a preferred fraction boiling between 375 degrees and 475 degrees F. through fractional distillation of a "sweetened" petroleum oil.

The ratios of the hydrocarbon solvents to the tung oil compositions were found to be variable between wide limits, but critical as to the upper limit of tung oil in the processing composition. Above 70% of oil the capacity to control the polymerization rate of the oil was rapidly decreased and became unduly difficult. At such percentages products of high viscosities were apt to result. The preferred solids content during solvent processing of the oil were within the range of from 50 to 60%. Lower solid content processing was objectionable only because of curtailed output and later complications introduced through the necessity of excess solvent removal. Above 70% solids (using a solvent processing method) the process failed to give consistent gas-proofing results.

Because of the low vapor pressure of the above defined hydrocarbon fractions useful in the treatment, additional research work disclosed that as low as 44% of the above defined fraction, which for brevity can be labelled a kerosene fraction, in conjunction with another low boiling solvent, e. g., mineral spirits, was more useful. The blend allowed faster solvent release from and consequently more rapid drying of the films deposited from treated oils.

Blends of various hydrocarbon solvents were found to be effective so long as at least 44% of the solvent blend employed as the processing solvent was a petroleum fraction boiling above the mineral spirits fraction (or from 350 degrees F. and upwards). A preferred solvent blend was found to contain 50% of kerosene and 50% of mineral spirits. In order that the bodying rate be properly controlled at least 30% of the solvent blend was refluxed with the conjugated oil during the processing steps. The only objection to the solvent process other than demand for special equipment and limitation as to solids content of the final processed conjugated oil was the slow release of the high boiling fractions in applied films of the treated oil in its ultimate use as a surface coating.

Shortly after the discovery of the success of the solvent processing method of altering the drying character of tung oil by, it is believed, an isomerization of the oil, experiments were begun to attempt to determine the nature of the active material in the petroleum fractions or "cut" between 350 degrees to 500 degrees F., which apparently catalyzed the isomerization of tung oil type drying oils to a more satisfactory and greatly improved drying oil.

Among the reasons considered for the activity of the aforesaid fractions in gas-proofing the oil was that the such fractions contained traces of elemental sulfur. The copper corrosion test, however, failed to show the presence of sulfur (see ASTM-D-235-39) and the Doctor Test (see ASTM-D-484-40) for the presence of mercaptans also gave a negative result. Sulfur in the elemental state and mercaptans were temporarily eliminated from consideration as possibilities.

Upon further investigation it was determined that the petroleum fractions which were obtained having boiling points within the range of from 350 degrees to 500 degrees F., were fractions that were essentially inert, saturated hydrocarbons free from aromatics. It was found that it was common practice to "sweeten" such petroleum distillates by treatment with sodium plumbate or cupric chloride solutions, known as "doctor solutions" which oxidized objectionable mercaptans to disulfides. It was also suggested that the Edeleanu process for refining kerosene has been used extensively, by which process aromatics are removed, and that in the more recent solvent extraction techniques aromatics are also removed from the less soluble aliphatic fractions. These processes gave strong indications that the active material present in the defined fraction were alkyl type materials having boiling points above 350 degrees F. It was strongly suspected that disulfides were present as a result of the "sweetening" process with the "doctor solutions." References indicated that dipropyl disulfide had a boiling point range of 288 to 290 degrees F., and was therefore considered to be below that which would be found in the distillate range which was of interest. Di-alkyl disulfides boiling above 350 degrees F. were considered to be those probably present in the selected petroleum fraction.

The evidence strongly indicated that dialkyl disulfides above dipropyl disulfide were the active catalysts present in the kerosene fraction which promoted the desired effect in the improvement of tung oil.

To eliminate one other possibility, elemental sulfur was tried and it was found that if more than 0.4% of elemental sulfur was added to the conjugated oil and the oil thermally processed in a non-reactive solvent such as mineral spirits, gas-proofing could be obtained, but that the drying rate of the resultant oil was greatly reduced. If the percentage of sulfur was dropped below 0.4%, the oil was not rendered gas-proof and not free from surface defect upon drying in their films.

Mercaptans were found upon trial to be useless for the purposes intended, except under particular conditions hereinafter mentioned.

A great number of additional organic sulfur compounds were investigated to determine if one of the group could supplant the materials occurring in the commercially available petroleum fractions above the mineral spirits range. Among those tested which were of little laboratory interest and did not lend themselves to commercial use were the following:

Thiophene
 Phenyl sulfide
 Tertiary aryl mercaptan
 Tertiary heptyl mercaptan
 Tertiary hexadecyl mercaptan
 Tertiary heptadecyl mercaptan
 Tertiary octadecyl mercaptan
 Tertiary dodecyl mercaptan
 Hydrogen sulfide
 Carbon disulfide
 Thiourea
 Thioglycol
 Thio beta naphthol
 Sulfur monochloride
 Zinc dimethyl dithio carbamate
 Di benzothiazyl dimethylthiourea
 Alkyl phenol sulfide

The following materials were found useful in laboratory tests, but because of their high cost, relative scarcity, and relatively poor result obtained as compared with other crystalline or amorphous compounds of this general class more readily available, and less difficult to handle, are not preferred.

Di (tertiary butyl) disulfide
 Di (tertiary amyl) disulfide
 Di (tertiary octyl) disulfide
 Diisopropyl dixanthogen
 Di (tertiary dodecyl) disulfide
 Di (tertiary tetradecyl) disulfide
 Tetramethylthiuramdisulfide

Extensive laboratory and plant tests, as a result of a preliminary screening of available disulfides indicated that the preferred compounds include the following:

Diphenyl disulfide
 Benzothiazyl disulfide (Thiofide, Monsanto Chemical Co.)
 Dibenzyl disulfide
 Di (1-hydroxy 4-amyl phenyl) disulfide (Vultac No. 2, Sharples Chemical Co.)
 Di (tertiary hexyl) disulfide
 Kerosene fraction from a "sweetened" petroleum oil.

From the evidence gathered it was plain that certain organic disulfides were capable of catalyzing changes in tung oil. The change was apparent in the freedom of the oil so treated from surface aberration when the oils were applied and dried in a film.

It was observed that while tertiary hexyl mercaptan was of no value, a derivative, ditertiary hexyl disulfide, upon comparison in practical tests, was found useful as a catalyst in the processing of tung oil. A test, based upon the sweetening of petroleum with doctor's solution, e. g., a sodium plumbate reagent, was followed. In this test, a catalytic amount of tertiary hexyl mercaptan containing a small amount of anhydrous sodium plumbate was added to tung oil and processed by thermal treatment. The result indicated that a mercaptan, previously proven valueless, could be oxidized in situ in the conjugated oil to a disulfide of the type heretofore found useful to produce a satisfactory gas-proof and wrinkle-free processed tung oil. A further test run using only the anhydrous sodium plumbate and tung oil under otherwise comparable conditions failed to effect gas-proofing of the dried film resulting therefrom. Further, anhydrous doctor's solution when incorporated in a tung oil varnish cook failed to effect gas-proofness of the dried film therefrom. It thereupon became evident that mercaptans could be oxidized in situ to form disulfides of practical value in gas-proofing tung oil. This was also a further indication that the active catalyst of the kerosene fraction was composed of dialkyl disulfides arising from the sweetening process in the preparation of certain petroleum distillates above the mineral spirits fraction.

It is well known that free sulfur or mercaptans present in petroleum fractions are rendered innocuous by oxidation with alkaline sodium plumbate or copper chloride "doctor" solutions. After treatment the sulfur compounds are converted to disulfides or polysulfides and although the sulfur content is not materially changed the form of the sulfur remaining is in more complex composition. As indicated, it was discovered

that long chain alkyl disulfides as well as aryl disulfides and aralkyl disulfides, if used in sufficiently small or catalytic proportions, could be added to solvents known to be inactive in effect upon China-wood oil, for example xylene, and achieve a non-frosting, essentially unbodied, and rapid drying China-wood oil.

In order to prepare catalytically active solvents of this nature it became desirable to use hydrocarbon fractions within lower boiling point ranges by the addition thereto of minor amounts of such active organic disulfides. By this additional improved step it was possible to eliminate the limitations previously inherent in the use of petroleum hydrocarbons in the kerosene range and above when such limitations (e. g. solvent retention) became objectionable.

It was also discovered that the solvent could be eliminated in certain operations and it was found that if additions were made to raw tung oil above .005% but not more than 0.1% of such an organic disulfide and the oil thereafter thermally processed between 440 degrees to 470 degrees F., equivalent improvement in the dry film characteristics of tung oil coatings could be obtained without the necessity of solvent processing.

It was further found that polymerization was sufficiently retarded in rate during open kettle operations that 100% tung oil modified alkyd type varnishes could be made successfully. Heretofore, in the manufacture of oil modified alkyds the practice had been limited to alkyds wherein at least a part of the modifying tung oil was replaced with a less reactive drying or semi-drying oil. Often linseed oil was used for this purpose. It was also found that oleoresinous varnishes based on rosin esters of polyhydric alcohols and tung oil could be made with certain qualities superior to varnishes of similar composition heretofore produced. Control of the final characteristics of the varnish, particularly as to viscosity and non-frosting qualities was made more certain through the use of minute amounts of the preferred additives hereinbefore disclosed.

Drying oil chemists are familiar with the fact that the increase in viscosity upon thermally processing tung oil is not a uniform function and that it is extremely difficult to promote alteration in the behavior of naturally conjugated drying oils at elevated temperatures within the ranges herein indicated without frequently completely gelling the entire mass. Therefore, means of selective retardation of the polymerization at such temperatures is a distinct advance in the art, particularly where the means does not retard the ultimate drying rate of the processed oil at room temperatures when applied in their films. This latter retardation is one of the chief objections to the use of phenols, beta naphthol, elemental sulfur, and other anti-oxidants heretofore suggested in the art.

So far as is known the prior art methods invariably have been limiting in the use for which the processed oil could be employed. Almost invariably the viscosity was increased to a considerable extent, and often upon treatment the tung oil would gel completely, resulting in a loss of material or a processed oil of a degraded value. Almost invariably, too, the drying rate suffered materially and in some cases the processed oil lost its drying quality.

If, on the other hand, the processes were modified to attempt to secure by obvious reductions

in the severity of the treatment, a modified result, and an oil of low body and unimpaired drying rate was obtained which would allow tack-free films of requisite hardness, the said oil films were found to retain the tendency to surface aberration, to wrinkle, gas-check or "frost." If one were to follow the teachings of the prior art, it would generally be found that gas-proofness, or freedom from surface aberration, is inversely proportional to the drying ability of the processed tung oil. That is, the more certain the process to produce a gas-proof oil the more slowly the oil would dry upon exposure to the air.

By our method, conjugated drying oils, which can be defined as natural conjugated vegetable (as opposed to animal) oils, are isomerized so as to prevent surface aberration in dried films of the said oils without materially altering the drying speed of such oils upon exposure, without necessarily materially increasing the body or viscosity of these oils, by treatment with certain organic polysulfides in catalytic amounts but not more than 0.1% by weight of the oil, either in a solvent process treatment or an open kettle treatment at temperatures broadly within the range of from 350 degrees to 525 degrees F. for from one to ten hours of processing time.

The following examples, in which the quantities are stated in parts by weight unless otherwise indicated, are illustrative of the manner in which the invention may be practiced.

Example I

300 parts tung oil
300 parts kerosene fraction of a sweetened petroleum oil

The above ingredients were placed in a three-neck glass flask equipped with thermometer, reflux condenser, and a source of inert gas, e. g., CO₂.

The mixture was heated to a temperature of 200 degrees C., and held for 5 hours. An oil resulted which was substantially unbodied (about the same as the original oil-kerosene mixture) which retained the fast drying character of tung oil. Upon incorporation of the usual amounts of conventional driers (e. g., cobalt, manganese and lead naphthenates) the surface of the dry film was found to be smooth and free from the usual surface aberration associated with tung oil films.

Example II

300 parts tung oil
132 parts kerosene fraction
168 parts mineral spirits fraction

The ingredients were processed together in apparatus identical to that used in Example I. The reflux temperature was reduced slightly due to the lower boiling mineral spirits, e. g. 195 degrees C.

The resultant oil was found to have gained no appreciable body, and upon drying in a thin film was free from gas-checking, wrinkling or frosting, and gave a clear, bright and smooth film which dried faster than the oil in Example I. The drying rate was increased due to the faster solvent evaporation of the mineral spirits fraction as compared with the results achieved in Example I.

Example III

300 parts tung oil
100 parts kerosene fraction
200 parts mineral spirits fraction

The foregoing ingredients were processed as in Examples I and II. The attempt was made to increase the rate at which solvent would vaporize from the film of oil. It was found that the resultant oil was not free of objectionable surface aberration of the light falling upon the film. The oil was subject to gas-checking, and the amount of catalyst was insufficient to alter the oil to improve its drying characteristics as to surface wrinkling.

Example IV

250 parts W. W. rosin
32.4 parts pentaerythritol
34.0 parts kerosene fraction

The above ingredients were weighed into a three-neck glass flask equipped with agitator, reflux condenser, water trap and thermometer. The mixture refluxed at 240 degrees C. and was held seven hours to an acid value of 10. 17 parts of water were collected in the side arm trap.

200 parts tung oil, and 20 parts mineral spirits were added, the reflux temperature was thereby reduced to 210 degrees to 220 degrees C., and the reflux continued for an additional three hours. The solids of the batch were reduced to 50% by addition of mineral spirits. The viscosity of the varnish was "E"- "F" on Gardner-Holdt tubes. The acid value was 9. The tung oil-rosin ester varnish after incorporation of driers dried to a smooth film, free of surface defects and was free from any tendency to gas-check.

The oil length of the varnish can be changed by adding additional tung oil in accordance with known calculations to produce a variety of oil-length varnishes, free of wrinkling, regardless of the length of the varnish.

By the above method, it is possible to make tung oil varnishes having less body, at lower temperatures and yet free from the expected surface defects, e. g. wrinkling, and gas-checking.

This example and Example III further illustrates that a certain amount of the catalytic factor present in kerosene must be present in order to gas-proof tung oil. If all mineral spirits are employed, the oil is not altered even though processed at the same temperature as in Example II. At 50% tung oil, 50% solvent concentrations, Example II illustrates the lowest concentration of the kerosene range distillate practicable for consistent results.

Example V

1000 parts tung oil
1 part diphenyl disulfide

The above ingredients were weighed into a stainless steel varnish kettle and the temperature of the batch increased to 440 degrees F., and held for one hour and a half, meanwhile maintaining an inert gas atmosphere over the batch. The resulting oil dried both with and without driers to a smooth, transparent film free from surface aberration. The same quality oil, similarly processed but without catalyst resulted in an extremely heavy viscosity material which was not free from gas-checking upon exposure to a gas-contaminated atmosphere during the drying period.

Example VI

1.5 parts ditertiary hexyl disulfide, and
1000 parts tung oil

The foregoing ingredients were processed as in Example V. A gas-proofed oil resulted, but the

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rate of bodying of the oil during treatment was accelerated objectionably during the process.

Example VII

1.0 part ditertiary hexyl disulfide
1000 parts tung oil

These ingredients were processed as in Example V. By reducing the amount of catalyst to 0.1% the bodying rate of the oil during treatment was not appreciably altered, and the oil dried to form a surface free from defect. Further experiment indicated that the bodying rate was at an optimum low at about 0.1% of added ditertiary hexyl disulfide catalyst.

Example VIII

1000 parts tung oil
1 part dibenzyl disulfide

The oil and catalyst were heated together in a stainless steel kettle blanketed with inert gas at a temperature of 475 degrees F. The resultant oil gave a slower drying oil than when heated at 450 degrees F., and the film was less tough after thorough drying. A similar test was made with identical ingredients at a temperature of 425 degrees F., holding the temperature for three hours and a half. The resulting oil was not gas-proofed and exhibited a frosty film after drying in a contaminated atmosphere. These tests indicate that optimum results as far as temperature is concerned lies in the range of from 440 degrees to 470 degrees F., where a non-solvent or open kettle processing step is employed.

Example IX

1000 parts tung oil
0.7 part di(4-amyli-1-hydroxyphenyl) disulfide (Vultac #2—a product of Sharples Chemical Co.)
660 parts mineral spirits

The above ingredients were weighed into a closed vessel fitted with a reflux condenser and a thermometer. After refluxing the mixture one and one-half hours at a moderate rate, the resultant oil was found to dry without surface aberration and when catalytic amounts of lead manganese and cobalt naphthenate driers were added the films were found to be without the usual defect of non-processed oil.

It is to be noted that mineral spirits alone will not alter the drying character of tung oil if used in an equivalent manner to the above example without the alkyl phenol disulfide added.

Example X

730 parts of tung oil and 500 parts of glycerine were charged into a stainless steel varnish kettle equipped with thermometer, inert gas blow ring and an agitator and under a light inert gas blow the batch was heated to 410 degrees F. A paste of a little of the oil and 0.85 part of litharge was added and the temperature increased to 440 degrees F., in a total time since the start of the cook of one hour. As a catalyst, 0.175 part of an alkyl phenol disulfide (Vultac #2—a product of the Sharples Chemical Co.) was then added and the temperature maintained at 440 degrees F., for three-quarters of an hour. 850 parts of phthalic anhydride were added and the blow with inert gas was increased to a moderate rate. The temperature was held at 440 degrees F., for a 15-second cure. The batch was reduced by dropping it into sufficient solvent to produce a 50% solids

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varnish. A hydrogenated petroleum fraction (Solvesso #1) was used as the solvent.

The resulting alkyd varnish, modified 100% with tung oil had a Gardner viscosity of Z₁—Z₂ and dried to a perfect surface free from optical aberration of light incident to it, after suitable quantities of paint driers had been added thereto (e. g., 0.5% lead, 0.05% manganese and 0.03% cobalt as the naphthenate salts).

Example XI

125 parts essentially neutral rosin-pentaerythritol resin ester
255 parts raw tung oil
0.13 part di(benzothiazyl) disulfide (Monsanto Chemical—Thiofide)

The resin and oil plus the catalyst were charged into a stainless steel kettle and heated to 440 degrees F., in one hour. The temperature was held at 440 degrees F., for approximately two hours, as determined by "cure" tests. The "cure" value was between 15-18 seconds. The viscosity at 50% solids with mineral spirits was between "E" and "G" on the Gardner-Holdt tubes. The cure point was determined by exposing a very small drop of the resin-oil under test to the surface of a hot plate maintained at a standard temperature of 392 degrees F. The time between the application of the drop and the time when the film starts to form gel particles is the cure point, usually expressed in seconds.

This example illustrates an open kettle preparation of an oleo-resinous tung oil varnish.

Example XII

2100 parts raw tung oil
401 parts dehydrated castor oil
0.5 part di(benzothiazyl) disulfide (Monsanto Chemical—Thiofide)
2080 parts mineral spirits

The above oils were charged into a stainless steel kettle along with the oil control catalyst, in this case di(benzothiazyl) disulfide was selected because of commercial availability. The log of the cooking procedure was as follows:

Time	Temperature	Cure Value
Fire on:	° F.	Seconds
9:05 a. m.-----	Room	-----
10:10 a. m.-----	450	-----
10:20 a. m.-----	450	73
10:45 a. m.-----	450	53
11:15 a. m.-----	450	35
11:25 a. m.-----	450	33
11:32 a. m.-----	450	26
11:40 a. m.-----	450	18

The batch was thereupon removed from the fire and cooled sufficiently, to allow reduction with mineral spirits.

After reduction the product had a viscosity of G-H (Gardner-Holdt) and solids of 55%. The resultant vehicle dried to a defect free film after incorporation of the usual driers. Without the addition of the control catalyst the above batch cannot be successfully cooked as appreciable quantities of skins and gel particles in the batch give rise to excessive losses.

The examples above illustrate both an open kettle method and a solvent process. By open kettle it is meant the usual varnish kettle which has not been equipped with a condenser by which reflux operations can be carried on. In the solvent process the same general equipment can be used if due care is shown to explosive hazards

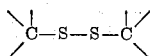
and the kettle fitted with a tight fitting cover equipped with suitable condensing means. In open kettle processing no solvent is used and the temperature is controlled principally by control of the heat input. In a solvent process the reflux of the volatile solvent serves as an auxiliary means of temperature control and to maintain an unreactive atmosphere over the cook.

While low boiling alkyl disulfides can be used with superatmospheric pressure equipment in processing conjugated oils as herein, the additional required capital investment is unnecessary in view of the results obtained at atmospheric pressures.

Where solvent processing is employed, it has been found that temperatures within the boiling point range of kerosene are broadly useful (e. g., 350 to 500 degrees F.) but in the open kettle method using the catalytic disulfide compound in a relatively pure form without a solvent, a more accurate temperature control has been found to be desirable. In this latter case, a range of from 440 degrees to 470 degrees F. is useful but 450 degrees to 455 degrees F. is preferred, as more satisfactory results are obtained in that range of temperature.

It is to be remarked that tung oils treated as shown in the examples will dry to handle in from one to one and one-half hours in the presence of the usual driers whereas prior art catalysts such as beta naphthol and phenolic treatment will retard the drying rate of tung oil processed with said materials. A minimum of two hours, and usually more time to dry, is required with such catalysts, whereas by the process herein shown, the treated oils will dry in less than two hours.

From the foregoing description it will be apparent that good results can be obtained in the treatment of tung oil, and other conjugated drying oils where the problem of surface aberration exists, with catalytic amounts of organic polysulfides containing the nucleus



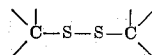
This nucleus is characterized by two divalent sulfur atoms linked to each other and to different carbon atoms. In the aromatic disulfides one or both carbon atoms in said nucleus are a part of a carbocyclic (e. g., phenyl, naphthyl) ring. In the alicyclic disulfides one or both carbon atoms of the nucleus are linked to an acyclic carbon chain which is attached to an aromatic ring (e. g., benzyl). In the heterocyclic disulfides, one or both carbon atoms of such nucleus are part of a heterocyclic ring (e. g., thiazyl, benzothiazyl, selenazyl, benzoselenazyl, oxazyl, benzoxazyl). In the cycloaliphatic disulfides, one or both such carbon atoms are part of a cycloaliphatic ring (e. g., cyclohexyl). In the aliphatic disulfides, one or both such carbon atoms are a part of an alkyl group (e. g., isopropyl, butyl, isoamyl, tertiary hexyl, tertiary tetradecyl, and homologues thereof). Although the disulfides present in kerosene fractions from sweetened petroleum have not all been definitely determined it appears that they are largely dialkyl disulfides in which the alkyl group contains at least three carbon atoms. The branched chain alkyl derivatives and the shorter alkyl chain derivatives (preferably less than eight carbon atoms) have given the best results among the dialkyl disulfides. It will be apparent that mixed alkyl-aryl disulfides and other types of mixed disulfides can be used.

By the term "varnish vehicle" as herein used it is meant to refer to a homogeneous transparent liquid which when applied in a thin film dries upon exposure to the air to a continuous film, said vehicle consisting of a combination of more than one of the following ingredients: resins, oils, driers, and thinners; and which dries through evaporation of solvent if solvent is present, oxidation and/or polymerization. The term "vehicle" alone is broader and may refer to a straight drying oil, or a drying oil and resin, or the reaction product of a number of ingredients to form an adhesive binder, capable of forming continuous films useful in paints, varnishes and other coating compositions.

Throughout the specification and claims the term "cure" point refers to a means of measuring the degree of polymerization of a mass undergoing such reaction. The measurement is made by exposing a drop of the reacting medium to the polished surface of a metal slab maintained at a constant temperature of 200 degrees C. (392 degrees F.). Immediately after the exposure of the drop to the hot surface it is spread out over the largest possible area with a pointed metal tool while at the moment of application of the drop a timer has been started. The film is spread continuously with the metal tool until gelation occurs and the time from application of the drop until gelation in the film is observed. This elapsed time is the "cure," and the smaller the cure value, the higher the degree of polymerization of the oil.

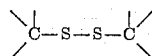
We claim:

1. A process of treating a conjugated drying oil which is normally subject to surface aberration comprising heating such oil to between 350 degrees F. and 525 degrees F. with a catalytic amount in the range of .005% to 0.1%, based on the weight of the oil, of an organic polysulfide containing the group



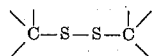
until said surface aberration characteristic is substantially inhibited.

2. A process of treating a conjugated drying oil which is normally subject to surface aberration comprising heating such oil with a catalytic amount in the range of .005% to 0.1%, based on the weight of the oil, of an organic polysulfide containing the group



at an isomerization temperature not less than 350 degrees F. nor exceeding 525 degrees F. in the presence of a vaporizable solvent for said oil until said surface aberration characteristic is substantially inhibited.

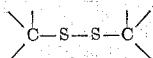
3. A process of treating a conjugated drying oil which is normally subject to surface aberration comprising heating such oil with a catalytic amount in the range of .005% to 0.1%, based on the weight of the oil, of an organic polysulfide containing the group



at an isomerization temperature not less than 350 degrees F. nor exceeding 470 degrees F. in the absence of any substantial amount of vaporizable solvent until said surface aberration characteristic is substantially inhibited.

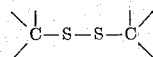
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4. A process of treating a conjugated drying oil which is normally subject to surface aberration comprising heating such oil to between 350 degrees F. and 525 degrees F. with a catalytic amount not exceeding 0.1%, based on the weight of the oil, of an organic polysulfide containing the group



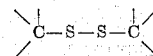
until said surface aberration characteristic is substantially inhibited.

5. A process of treating a conjugated drying oil which is normally subject to surface aberration comprising heating such oil to between 350 degrees F. and 525 degrees F. with a catalytic amount in the range of .005% to 0.1%, based on the weight of the oil, of an organic polysulfide containing the group



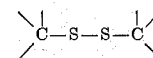
until said surface aberration characteristic is substantially inhibited.

6. A process of treating a conjugated drying oil which is normally subject to surface aberration comprising heating such oil to between 350 degrees F. and 525 degrees F. with a catalytic amount in the range of .005% to 0.1%, based on the weight of the oil, of an organic polysulfide containing the group



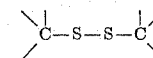
until said surface aberration characteristic is substantially inhibited, the carbon atoms of said group each forming a part of an aromatic ring.

7. A process of treating a conjugated drying oil which is normally subject to surface aberration comprising heating such oil to between 350 degrees F. and 525 degrees F. with a catalytic amount in the range of .005% to 0.1%, based on the weight of the oil, of an organic polysulfide containing the group



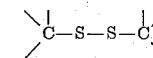
until said surface aberration characteristic is substantially inhibited, the carbon atoms in said group forming a part of a thiazole ring.

8. A process of treating a conjugated drying oil which is normally subject to surface aberration comprising heating such oil to between 350 degrees F. and 525 degrees F. with a catalytic amount in the range of .005% to 0.1%, based on the weight of the oil, of an organic polysulfide containing the group



until said surface aberration characteristic is substantially inhibited, the carbon atoms in said group each forming a part of an alkyl group.

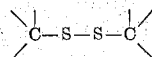
9. A process of treating a conjugated drying oil which is normally subject to surface aberration comprising heating such oil with a catalytic amount in the range of .005% to 0.1%, based on the weight of the oil, of an organic polysulfide containing the group



at a temperature in the range 425 degrees F. to 525 degrees F. in the presence of a vaporizable solvent for said oil, for one to ten hours.

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10. A process of treating a conjugated drying oil which is normally subject to surface aberration comprising heating such oil with a catalytic amount in the range of .005% to 0.1%, based on the weight of the oil, of an organic polysulfide containing the group



10 at a temperature in the range from 440 degrees F. to 470 degrees F., for one to ten hours.

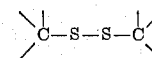
11. A process of treating a conjugated drying oil which is normally subject to surface aberration comprising heating such oil to between 350 degrees F. and 525 degrees F. with a catalytic amount not exceeding 0.1%, based on the weight of the oil, of di(benzothiazyl) sulfide until said surface aberration characteristic is substantially inhibited.

12. A process of treating a conjugated drying oil which is normally subject to surface aberration comprising heating such oil to between 350 degrees F. and 525 degrees F. with a catalytic amount not exceeding 0.1%, based on the weight of the oil, of diphenyl disulfide until said surface aberration characteristic is substantially inhibited.

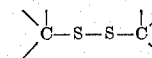
13. A process of treating a conjugated drying oil which is normally subject to surface aberration comprising heating such oil to between 350 degrees F. and 525 degrees F. with a catalytic amount in the range of .005% to 0.1%, based on the weight of the oil, of a dialkyl disulfide until said surface aberration characteristic is substantially inhibited.

14. The process of claim 13 in which a kerosene fraction containing a dialkyl disulfide is used.

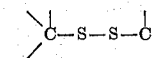
15. An open kettle method of manufacture of a tung oil modified varnish vehicle which comprises heating the said oil and its oil modifying resinous components to a temperature within the range of from 440 degrees F. to 470 degrees F. in the presence of a catalytic quantity but not more than 0.1% by weight of an organic disulfide containing the group



16. An open kettle method of manufacture of tung oil modified varnish vehicle which comprises heating the said oil and oil modifying components of the varnish to a temperature within the preferred range of from 440 degrees F. to 470 degrees F. for from one to four hours in the presence of a catalytic quantity but not more than 0.1% by weight of an organic disulfide containing the group



17. A solvent process for the manufacture of a tung oil modified varnish whose dried films are characterized by freedom from surface aberration which comprises refluxing the said oil in conjunction with oil modifying varnish forming ingredients within a temperature range of from 425 degrees to 525 degrees F., for from one to ten hours in the presence of a solvent for the oil and a catalytic quantity, but not more than 0.1% by weight, of at least one of the class of organic disulfides containing the group

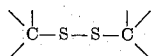


18. A solvent process for the manufacture of

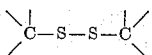
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tung oil vehicles to render the dry films resulting from said vehicles free from surface aberration which comprises refluxing the said oil-reactant mixture comprising not more than 70% of the said tung oil composition and at least 30% of a volatile solvent therefore, more than 16% of the said solvent being a sweetened petroleum fraction boiling within the range of from 350 degrees to 500 degrees F., and containing traces of organic disulfides present in said petroleum fraction.

19. A conjugated drying oil comprising essentially a conjugated drying oil and a catalytic amount not less than .005% and not more than 0.1% by weight of an organic polysulfide containing the group



20. An open kettle method of manufacture of a tung oil modified vehicle which comprises heating the said oil and its oil modifying components to a temperature within the range of from 440 degrees F. to 470 degrees F. in the presence of a catalytic quantity but not more than 0.1% by weight of an organic disulfide containing the group



21. A conjugated drying oil comprising essentially a conjugated drying oil and a catalytic amount not less than .005% and not more than 0.1% by weight of dibenzothiazyl disulfide.

22. A conjugated drying oil comprising essentially a conjugated drying oil and a catalytic

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amount not less than .005% and not more than 0.1% by weight of diphenyl disulfide.

23. A conjugated drying oil comprising essentially a conjugated drying oil and a catalytic amount not less than .005% and not more than 0.1% by weight of a dialkyl disulfide.

24. A conjugated drying oil comprising essentially a conjugated drying oil and a catalytic amount not less than .005% and not more than 0.1% by weight of dibenzyl disulfide.

25. A conjugated drying oil comprising essentially a conjugated drying oil and a catalytic amount not less than .005% and not more than 0.1% by weight of di(4-amyl-1 hydroxy phenyl) disulfide.

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EDWARD B. LUKAS.

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