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PREPARATION OF SOLUBLE OIL

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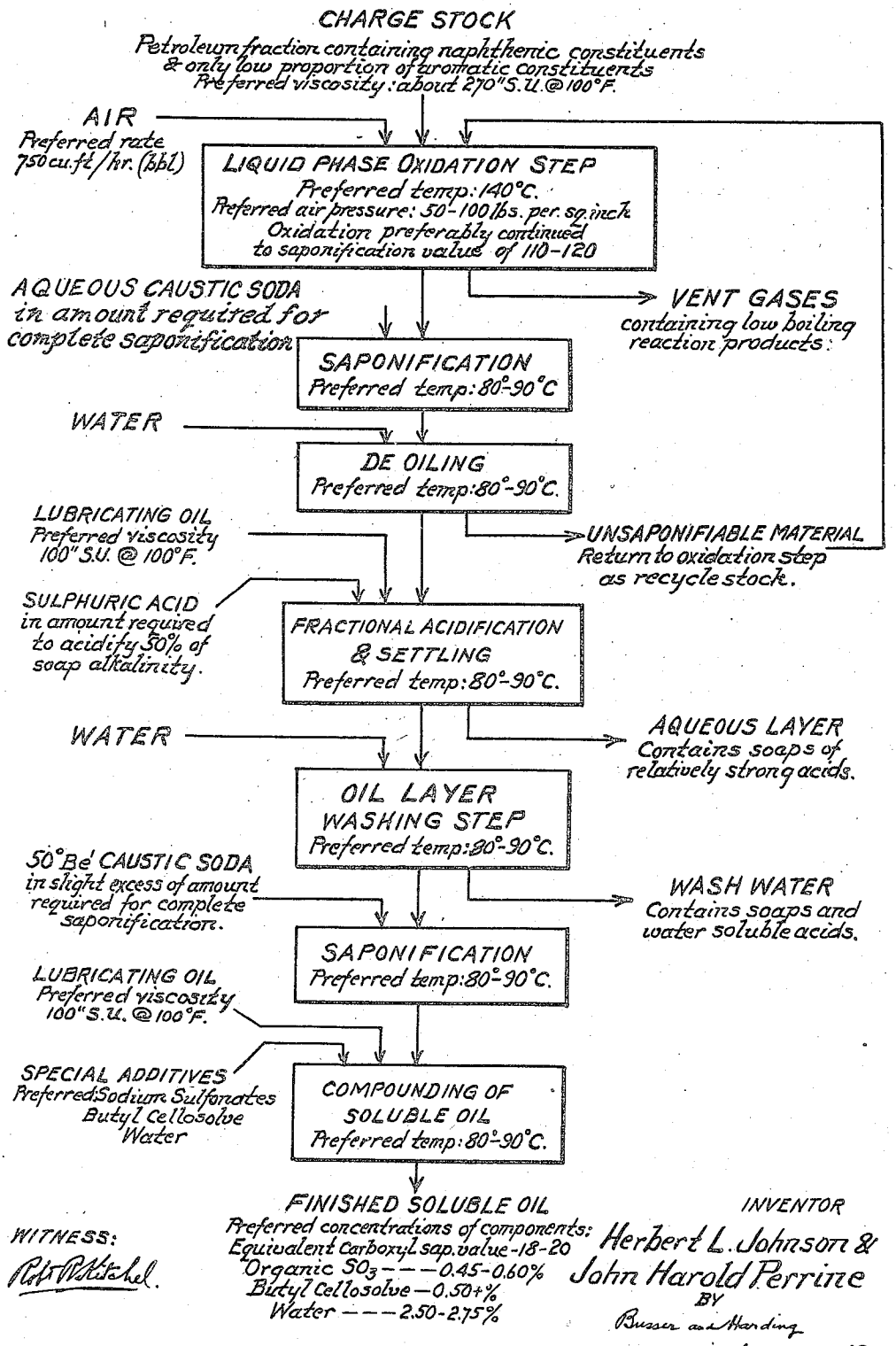

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PREPARATION OF SOLUBLE OIL

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This invention relates to soluble oils and to the preparation thereof from petroleum hydrocarbon starting materials, and more particularly is directed to a method of manufacturing soluble oils from petroleum fractions containing naphthenic hydrocarbons, which comprises partial oxidation of such fractions under selected operating conditions followed by a novel combination of interdependent and cooperating purification steps resulting in a refined stock particularly suited for compounding high-grade soluble oils.

The so-called soluble oils, which comprise homogeneous mixtures of oil and emulsifying agent, constitute a well recognized and distinct type of product. They are distinguished from oils such as used for engine lubrication particularly in that they have capacity for dilution with water to form oil-in-water emulsions whereas engine lubricants do not possess this characteristic. The soluble oils are used widely in the arts as cutting oils, spray oils, rust-proofing oils or the like. In such applications the oil is employed in aqueous dilution in the form of an oil-in-water emulsion. Probably the widest application for soluble oils is as cutting oils in metal working operations, such as cutting, grinding, boring, grooving, cold-drawing and the like, in which the oil-water dispersion serves the two-fold purpose of a lubricant and a coolant for the metal being fabricated. Among the essential requirements of high-grade cutting oils may be mentioned the ability of the undiluted oil to remain homogeneous under storage conditions, the ability to form exceedingly stable oil-in-water emulsions, non-corrosiveness to metal and, in addition, the ability to inhibit rusting of the metal under service conditions.

It is known to partially oxidize petroleum hydrocarbon fractions in both liquid and vapor phase, and it is well recognized that such oxidation results in a very complex mixture comprising unoxidized hydrocarbons, alcohols, aldehydes, ketones, carboxylic acids of both high and low molecular weights, oxycarboxylic acids, esters, lactones and the like. These complex oxidation mixtures thus contain many types of organic constituents which undoubtedly would have many useful applications in the arts, either as fractions of relatively pure chemical type or as mixtures of various types having characteristics desirable for specific purposes, provided the proper segregation of components into fractions could be effected. However, due to the complexity of the oxidized material, not only has resolution of the mixture into fractions of relatively pure chemical type so far proved to be impossible, at least on a commercial scale, but also the segregation of fractions having properties suitable for various specific uses heretofore has been exceedingly difficult to accomplish and in most cases impractical as a commercial operation.

It also is known to prepare soluble oils from certain naturally occurring petroleum acids, commonly called naphthenic acids. U. S. Patent No. 2,056,913, issued to Terrell et al., describes a method of recovering such acids and preparing soluble oils therefrom. However, as far as applicants are aware, no process of commercial value has been known heretofore for preparing high-grade soluble oils from synthetic acids derived by partial oxidation of petroleum hydrocarbons. Previous failure to provide a commercially successful process no doubt has been due to the complexity of the oxidized mixture, i. e. the presence of difficultly separable types of compounds having characteristics detrimental to soluble oils along with the desired components.

The present invention provides a commercially feasible process of oxidizing petroleum hydrocarbons and separating from the oxidation product an acidic fraction in which detrimental constituents are substantially absent and which therefore may be used to prepare soluble oil of highest quality. The process comprises a series of interrelated steps, each of which functions as a part of a unitary procedure and contributes to the success of the process as a whole.

More specifically, the present invention provides a method of producing soluble oil, which includes the following procedural steps in the order named:

(1) Liquid phase oxidation of petroleum fraction
(2) Saponification of the oxidation product
(3) Deoiling of the saponified material
(4) Fractional acidification of the deoiled saponified material
(5) Water washing the acidic fraction
(6) Saponification of the washed acidic fraction
(7) Compounding of soluble oil

With the exception of step 3, all steps are so vital to the successful production of high quality soluble oil that the elimination of any one step will result in failure of the process. Also substantial variations in operating conditions as set forth hereinafter likewise may cause failure. Although step 3 may be omitted without affecting the quality of the final product, its inclusion is highly desirable for economic commercial operation, as hereinafter more fully explained.

For a general understanding of the process to which this invention is directed, reference should be had to the accompanying drawing which diagrammatically illustrates the procedural steps. The process preferably is carried out in a batch-wise manner and will be described as such herein, although, as will be obvious to those skilled in the art, it may be conducted also as a continuous process.

The first step in the process comprises subjecting a charge stock to liquid phase partial oxidation in the absence of a special catalyst. Preferably fresh charge stock, comprising a mineral oil meeting certain specifications as hereinafter set forth, is blended with unsaponifiable material separated from a previous batch of oxidized oil, hereinafter referred to as recycle stock, and the blend is oxidized at a temperature of 130–150° C., preferably 140° C., by blowing therethrough and intimately contacting therewith a free-oxygen containing gas, preferably air, under a super-atmospheric pressure, preferably 50–100 pounds per square inch gauge. A stream of vent gases, containing the lowest boiling oxidation products, is withdrawn from the oxidation zone continuously throughout the oxidation period and may be passed to a condenser or other suitable equipment for recovery of the contained oxidation products. The oxidation preferably is continued until the batch has a saponification value of 110–120 mg. KOH/gram, the corresponding acid number being about 50–55, at which point the maximum yield of desirable reaction products is reached. The resulting mixture, comprising oxidation products of numerous chemical types and unoxidized oil, is treated with a strong aqueous solution of an alkali metal hydroxide, preferably caustic soda, in the theoretical amount required for complete saponification. Mixing is effected at sufficiently high temperature, preferably 80°–90° C., and for sufficient length of time to saponify all the esters and other difficultly saponifiable constituents, complete saponification being very important for obtaining a product suitable for producing high-grade soluble oils. After complete saponification the soap-oil mixture is diluted with a relatively large proportion of water, preferably three volumes of water being added for each volume of the oily mixture of products from the oxidation step, and the resulting mixture is allowed to settle, preferably at a temperature of 80°–90° C., until a clean separation of aqueous and oil phases is obtained. Soaps of relatively low molecular weight acids act here as de-emulsifying agents and play a major role in effecting a sharp separation of the two phases. The oil phase, comprising unoxidized oil and unsaponifiable water-insoluble oxidation products such as alcohols, aldehydes and ketones, separately is withdrawn and returned as recycle stock to the oxidation step, where it is blended with fresh charge stock and further subjected to oxidation. As later shown, this recycle stock has a catalytic effect in the oxidation step and serves to promote the desired oxidation reaction.

It is noted that the aqueous soap layer resulting from the deoiling step, even though a clean separation between aqueous and oil phases is obtained by virtue of the de-emulsifying effect of low molecular weight soaps, nevertheless contains a certain amount of unsaponifiable material (i. e. unoxidized oil, alcohols, aldehydes, ketones, etc.) dissolved or dispersed therein. As more fully explained later, this unsaponifiable material has been found to be not only beneficial but even necessary for compounding soluble oil of the highest quality from the product resulting from the subsequent purification steps.

The next step in the process comprises subjecting the aqueous soap layer to partial or fractional acidification, preferably at a temperature of 80°–90° C. Prior to carrying out this operation, it is desirable, although not requisite, that a light lubricating oil of the type to be used in the final step of compounding the soluble oil, for instance a distillate oil having a viscosity of 100 seconds S. U. at 100° F., be added to facilitate separation of layers in both the present step and the subsequent water washing step. The added oil promotes the separation mainly by lowering the specific gravity of the resulting synthetic acid layer, which otherwise would have a gravity of approximately 0.98, if preferred starting material had been used, or in other words not considerably less than that of the aqueous phase. A suitable amount of such oil to add is that equal in volume to the fresh charge stock which has been subjected to oxidation. After such addition, the mixture is subjected to fractional acidification by treating with a strong mineral acid, preferably sulfuric acid, in amount sufficient to acidify only a fraction of the soaps. The correct proportion of mineral acid to use depends somewhat on the particular conditions obtaining in the oxidation step and the degree of oxidation effected, especially on the proportion of oxy-acids formed. For the preferred conditions, the correct proportion is that equivalent to about 50 per cent of the alkali employed in the saponification, or in other words an amount of mineral acid equivalent to only about 50 per cent of the carboxyl groups. It has been discovered that such partial or fractional acidification selectively converts to acids the soaps of the weaker acids, i. e. of those having the lower dissociation constants, while leaving soaps of stronger acids unaffected. It also has been discovered that these stronger acids, comprising the lower molecular weight acids and oxy-acids, are highly detrimental and therefore must be substantially absent from the purified product from which soluble oil of the present invention is compounded. After partial acidification, the mixture is allowed to settle, preferably at 80°–90° C., until a clean separation is obtained. As in the preceding deoiling step, soaps of the low molecular weight acids serve as de-emulsifying agents. The resulting lower layer, comprising an aqueous solution or dispersion of soaps of the stronger acids (low molecular weight acids and oxy-acids) and, in addition, any water-soluble unsaponifiable products of the oxidation such as low molecular weight alcohols, aldehydes or ketones not removed in the vent gases from the oxidation step, is drawn off and either discarded or separately processed for recovery of contained oxidation products.

The upper layer comprises a mixture of the weaker carboxylic acids and oil and, in addition, contains some soaps as well as some water-soluble free acids as contaminants. These soaps and water-soluble acids, although present in relatively small amounts, would be highly detrimental if allowed to remain in the mixture and so must be removed before compounding of the soluble oil. This is accomplished by agitating the layer, preferably still at 80°–90° C., with an equal volume of water, allowing the resulting mixture to stratify and withdrawing the aqueous layer with

the said contaminants dissolved therein. The removed aqueous layer may be added to the soap layer obtained after the fractional acidification step and separately processed therewith or may be discarded. The washed oily layer may contain some water in suspension which may be removed by blowing with air.

The refined synthetic acid product resulting from the above outlined procedure is a particularly suitable stock for compounding soluble oil of excellent quality according to the formula and procedure hereinafter disclosed and described. It also may be used for preparing products of various other types such as greases, metallic derivatives for color lakes, siccatives or organic salt catalysts.

The starting material of the process outlined above consists of a petroleum fraction of lubricating oil consistency, containing a sufficient proportion of naphthenic constituents so that an average of at least one naphthene ring per molecule obtains. The naphthenic constituents are desirable in order that the acidic product obtained by oxidation and subsequent purification will resemble natural naphthenic acids rather than fatty acids, since naphthenic acids have characteristics making them more suitable than fatty acids for the production of soluble oils of the type herein concerned. More particularly, soluble oils prepared from naphthenic acids should be slightly alkaline for best results whereas those prepared from fatty acids should be acidic (i. e. containing free fatty acids). Since the desired product of the present invention is the alkaline type soluble oil, it accordingly is desirable that the synthetically produced acidic material resembles natural naphthenic acids in this respect. The desirability of having sufficient naphthenic components in the starting material does not necessitate the use of petroleum fractions derived only from the so-called naphthenic base crudes, although these are preferable, for in many cases fractions derived from either mixed base or paraffin base crudes contain sufficient naphthenic components to be useful.

Another prerequisite of the starting material is that it should not contain more than a certain maximum concentration of aromatic components. It has been found that aromatics greatly increase the resistance of the oil to oxidation, apparently having an inhibiting effect on the oxidation of the other types of components present. When sufficiently severe oxidizing conditions are employed to force oxidation of highly aromatic oils, there is a tendency toward the formation of sludge rather than the desired oil-soluble acidic reaction products. The maximum concentration of aromatics, above which the desired oxidation cannot be effected, depends on two factors. First, the maximum allowable concentration is related to the molecular weight of the starting material; the lower the molecular weight the greater being the allowable concentration. Second, it also depends on whether or not recycling is employed, i. e. whether or not unsaponifiable material after being separated from the oxidation product is returned to the oxidation step along with fresh charge stock, as described above. By way of illustration of these factors, the following concentrations of aromatic rings, as determined by the Watermann method, have been found allowable for obtaining satisfactory oxidation rates:

	Proportion of aromatic rings
270 S. U. viscosity stock without recycle	Not over 4%
270 S. U. viscosity stock with recycle	Not over 7%
Kerosene with recycle	Not over 16%

The synthetic acids resulting from the oxidation and purification procedure described above have been found to have about the same average molecular weight as the starting material used. The selection of a suitable starting material therefore should be made on the basis of the molecular weight desired for the product. For petroleum fractions derived from naphthenic base crudes, a viscosity range of 150–350 seconds S. U. at 100° F. corresponds to a molecular weight range suitable for the preparation of soluble oils according to the invention, although the preferred viscosity of the starting material is about 270. Low molecular weight fractions, such as kerosene, give reaction products of too low molecular weight to be suitable in the present application.

Most petroleum fractions of suitable molecular weight range, which have been obtained from crude petroleum by the usual distillation procedure without further treatment, contain too high an aromatic content to be useful per se as charge stock for the process and therefore require pretreatment to reduce the concentration of aromatics therein. Any suitable pretreatment whereby the concentration of aromatics is reduced sufficiently may be used; for instance, solvent extraction or treatment with concentrated or fuming sulfuric acid may be employed. The latter method, which has been used widely in the arts for the production of so-called white oils, is a convenient means of preparing suitable charge stock. For instance, a 270 viscosity oil fraction derived from a naphthenic base crude of the Gulf Coastal type may be treated at 70° F. in the conventional manner with 160 pounds of 20 per cent fuming sulfuric acid per barrel in increments of 20 pounds per barrel to yield a stock having particular utility as starting material and showing the following composition by Watermann analysis:

	Per cent
Aromatic rings	1
Naphthenic rings	59
Paraffinic chains	40

It is noted that for any given oil the refractive index of the oil affords a convenient means of determining when the aromatic content is sufficiently low, and is used in preference to the somewhat difficult Watermann analysis method as a means of routine control of the pretreating step. Thus for an oil such as the above, a refractive index below 1.4890 indicates that the oil may be oxidized without the addition of recycle stock, an index of 1.4890–1.4920 indicates that the oil will oxidize satisfactorily if mixed with recycle stock, and an index above 1.4920 indicates that the oil will not oxidize properly even if recycling is employed.

In the oxidation step the main factors affecting the rate of oxidation, besides the aromatic content of the charge and the effect of recycling as indicated above, are pressure and temperature. The air rate appears to have little effect provided the exit or vent gas contains a substantial percentage of free oxygen. In order to ensure a practical oxidation rate, the pressure should be

maintained above atmospheric pressure, generally above 25 pounds per square inch gauge, but not in excess of about 175, and preferably should be 50–100. At the preferred temperature a pressure below about 25 gives a rate of oxidation which is too slow to be practical. As the pressure is increased, the reaction rate also increases until a pressure of about 100 pounds per square inch is reached; whereupon further increases cause the rate to diminish, until at a pressure exceeding about 175 the rate again has become undesirably slow. It has been discovered that this decrease in rate at pressures above about 100 pounds per square inch is due to retention of low boiling oxidation products in the reaction mixture and that such products retard or inhibit the oxidation reaction. At lower pressures these low boiling products, on forming, rapidly are removed in the vent gas and so do not affect the reaction rate appreciably.

The temperature at which the oxidation suitably may be carried out is confined to a relatively narrow range. With a charge stock such as the one described above, a temperature of approximately 140° C. gives the best results although any temperature within the range of about 130°–150° C. may be used. Below this range, for example at 120° C., the rate of oxidation is exceedingly slow; on the other hand at temperatures above about 150° C., say at about 155° C. and higher, there is formed an undesirable oil-insoluble sludge-like product having no utility in the present application. The optimum temperature and the limits of temperature for practical commercial operation may vary somewhat, depending on the composition and molecular weight of the charge stock, and therefore a definite optimum temperature or the limits of temperature suitable for all charge stocks cannot be specified. In all cases, however, the temperature should be sufficiently high to give a commercially practical rate of oxidation but not so high as to cause the formation of sludge-like products. It appears that temperatures lower than about 120° C. or higher than approximately 165° C. are seldom if ever suitable.

It obviously is desirable that the oxidation be carried to such a degree as to effect maximum yield of the desired product, and it has been found that this maximum is obtained when the oxidized oil reaches a saponification value of about 110–120 at which point the corresponding acid value is about 50–55. It is permissible to stop the reaction at any point short of this degree of oxidation provided the product obtained from the subsequent purifying procedure has a saponification value sufficiently high to produce soluble oil according to the formula hereinafter disclosed; for instance, the reaction might be stopped when the saponification value is even as low as about 30. This is undesirable, however, for economic commercial operation. Likewise the oxidation may be continued for a substantial extent past the point of maximum yield, and by appropriately adjusting conditions in the subsequent purification steps a purified product suitable for compounding soluble oil may be obtained in relatively low yield. The decrease in yield on continuing the oxidation past a saponification value of 110–120 is due to the increased formation of oxy-acids which have been found to be highly detrimental in soluble oil manufactured in accordance with this invention. These oxy-acids are soluble in the reaction mixture and so remain dissolved therein during the oxidation, but are insoluble in light petroleum hydrocarbons, for instance, in pentane, and may be precipitated from the reaction mixture by diluting the mixture with pentane or other light hydrocarbons. This affords a convenient way of determining the concentration of such oxy-acids. When a preferred charge stock as described above was oxidized to various degrees and the reaction mixtures were diluted with twice their volumes of pentane, the following approximate percentages of pentane-insoluble products were obtained:

Saponification value of reaction mixture, mg. KOH/g.	Percent pentane-insoluble products
60	1
80	3
100	7
120	12
140	19
160	28
180	38

Although these values for pentane-insoluble products probably include small percentages of low molecular weight acids such as acetic acid, propionic acid, etc., which are present in minor proportions and would be insoluble in pentane, nevertheless they may be taken as approximate indications of the oxy-acid concentration. These pentane-insoluble oxy-acids are viscous, oily products having a clear, deep red color, and should not be confused with the oil-insoluble sludge-like products caused by too high oxidation temperature as referred to above. The tabulated data indicate that no more than about 10 per cent oxy-acids are present at the degree of oxidation corresponding to maximum yield (110–120 saponification value) but that further oxidation causes rapid increase in the proportion of these undesirable reaction products. Such larger proportions, although being undesirable, are permissible to an extent provided conditions in the subsequent fractional acidification step are so adjusted as to avoid acidification of the oxy-acid soaps and thus allow these components to be substantially removed from the desirable oxidation products.

When the oxidation is carried to a degree considerably beyond that contemplated by the present invention, a point eventually is reached at which incipient separation of highly oxygenated acidic products from the reaction mixture will occur. These highly oxygenated, reaction mixture-insoluble products are not the same type products as the oxy-acids referred to above but represent a higher degree of oxidation. The point of incipient separation, which will not be reached at a saponification value even as high as 180, corresponds to a much more severe oxidation than is embraced by the present invention.

All of the steps in the process following the oxidation step may be carried out at a temperature below that used in the oxidation, and preferably are carried out at a temperature below the boiling point of water in order that the processing equipment need not withstand pressure. As described above the first purification step comprises saponification, and in this step it is important that a relatively high temperature, say 80°–90° C., be employed in order to effect complete saponification of the oxidation product. It is desirable that all subsequent operations be performed at approximately this same temperature level so that adjustment of temperature between steps is eliminated. However,

after saponification, somewhat lower temperatures may be employed in the purification steps if desired, although this usually tends to lengthen the time required for mixing and settling operations.

In the saponification step following oxidation it is requisite for successful production of high quality soluble oil that complete saponification be effected. Since ester-like oxidation products are the last to saponify, incomplete saponification will result in substantial amounts of esters remaining in the saponified mixture; and although a major proportion will be removed in the deoiling step as recycle stock, the final product will contain an appreciable concentration of esters. It has been found that these esters are highly deleterious to the soluble oil, in that they undergo delayed hydrolysis on prolonged standing of the soluble oil, that is, they slowly hydrolize to the corresponding acids and alcohols, and in so doing eventually cause the soluble oil to change from slightly alkaline to acidic with a resultant considerable depreciation in the emulsion stability characteristics. If, through incomplete saponification here, esters are permitted to be present in the product from the purification steps but this ester-containing product is completely saponified in the step which just precedes the final compounding step thereby destroying all esters, nevertheless the desired soluble oil quality will not be attained due to the presence in the soluble oil of an appreciable proportion of low molecular weight soaps derived from the esters. In order to effect complete saponification, a strong aqueous solution of alkali such as caustic soda is added in amount calculated from the saponification value for exact neutralization and the mixture is agitated at 80°–90° C. until complete saponification is obtained. An excess of alkali may be added but this is not necessary and merely results in an increased consumption of both alkali and the mineral acid required in the fractional acidification step. It is desirable for the mixture during agitation to have a water content of about 10–20 per cent; this ensures fluidity and facilitates intimate mixing. If air blowing is used as a means of agitation, water may be added from time to time to compensate for that lost through evaporation.

The saponified mixture contains a large proportion of unsaponifiable material comprising unoxidized oil, alcohols, aldehydes, ketones and the like. It obviously is desirable that this unsaponifiable material be separately recovered in order to provide recycle stock which, as has been explained, has a beneficial effect in the oxidation step, as well as to decrease the consumption of fresh charge stock per unit volume of soluble oil produced, since the fresh charge stock due to the intensive pretreatment usually required represents a considerable fraction of the cost of the process and any saving in this starting material consequently is of considerable advantage. In order to separate a substantial proportion of the unsaponifiable material it has been found necessary to dilute the saponified mixture with water, otherwise substantially no separation is obtained. The following tabulation serves to show the effect of degree of dilution on the proportion of unsaponifiable material recovered after settling the diluted mixture for one-half hour at 80°–90° C.:

Volumes of water added per volume of saponified mixture	Unsaponifiable material recovered, per cent on charge to oxidation step
0	0
1	44.5
2	48
3	49.5
4	50

It is noted that no appreciable increase in recovery is obtained by diluting with more than about three volumes of water for each volume of saponified mixture. This proportion therefore is preferred. As previously pointed out soaps of relatively low molecular weight acids prevent emulsification and ensure separation of layers. Although a sharp separation is obtained, the resulting soap layer contains unsaponifiable material in amount equivalent to about 10 per cent of the charge to the oxidation step. It has been found that this unsaponifiable material later is beneficial in that it improves compatibility between the synthetic acids and hydrocarbon oil, improves compatibility between soaps of the acids and such oil, and improves emulsibility of the soluble oil product. If this 10 per cent unsaponifiable material is removed from the soap layer, for instance by extraction with a low boiling naphtha, before further processing, the final soluble oil product will have definitely poorer emulsion stability characteristics than otherwise.

In the fractional acidification step it is of prime importance that the proper proportion of mineral acid be added. If too small a proportion is used, a low yield of desirable product will result; on the other hand, if too large a proportion is used, the resulting product will contain acids having relatively strong acidic properties, which is highly undesirable since the soaps of such acids tend to be oil-insoluble and cause gelation as well as poor emulsibility of the final soluble oil. The correct proportion of mineral acid to use depends mainly on the amount of oxy-acids formed during oxidation, and also may depend to an extent on the particular pressure employed in the oxidation step, since the retention of the very low boiling acidic products is related to this factor. When the oxidation is effected under the preferred pressure and is carried to a degree corresponding to a saponification value of 110–120, a proportion of mineral acid equivalent to about 50 per cent of the carboxyl groups should be used. Also, since there is little difference in the percentage of oxy-acids formed for lower degrees of oxidation, about the same proportion of mineral acid is required when the oxidation is stopped at saponification values below 110–120. However, for higher saponification values, correspondingly smaller proportions of mineral acid are required due to increased percentages of oxy-acids.

It has been found that complete removal of the undesirable components does not result when the fractionally acidified mixture is allowed to separate into aqueous and oily layers and the aqueous layer is withdrawn. Instead the oily layer contains an appreciable amount of undesirable components, comprising water soluble acids and soaps of relatively strong acids, which must be removed in order to yield a product suitable for making high quality soluble oil. Substantially complete removal of these undesirable constituents is ef-

fected in the water washing step as described above. Although there is a tendency toward emulsion formation in this step since only a small amount of relatively low molecular weight soaps having de-emulsifying properties are present, troublesome emulsification is minimized or substantially eliminated by using a volume of water not considerably greater than the volume of the oily layer, preferably an approximately equal volume. The resulting refined product has a saponification value of about 49 and an acid value of about 30, provided that the oxidation has been carried to a saponification value of abcut 110, that 50 per cent of the mineral acid required for complete acidification in the fractional acidification step has been used and that lubricating oil has been added in amount equal to the desirable synthetic acids. The difference between saponification and acid values indicates the presence of some difficultly neutralizable constituents, believed to be lactones, the soaps of which readily are formed in the subsequent saponifying step. It should be understood that these lactones, although they represent a higher degree of oxidation than simple carboxylic acids, are not the same as the oxy-acids referred to above, but, in contradistinction to said oxy-acids, are substantially pentane-soluble and form soaps which appear to have a beneficial rather than detrimental effect on the quality of the finished soluble oil.

The last step in the process before finally compounding the soluble oil comprises saponification of the refined stock resulting from the above described purification procedure. This is accomplished by mixing the refined stock with a strong aqueous solution of an alkali metal hydroxide, preferably with 50° Bé. caustic soda, at 80°–90° C. and for sufficient time to effect substantially complete saponification. A small excess of alkali is used so that the finally compounded soluble oil will be slightly alkaline, preferably so that it will have a free alkalinity equivalent to 0.01-0.10% NaOH. It has been found to be of prime importance that this saponification be carried out before the refined stock is blended with other ingredients of the soluble oil; for otherwise, the compounded soluble oil on standing may exhibit gelation. No reason is apparent as to why the specific order of saponification followed by blending is of such importance; nevertheless, it has been found effective as a means of avoiding this undesirable gelation tendency.

The final step of compounding the soluble oil comprises blending the saponified stock, suitably at 80°–90° C., with lubricating oil and various special ingredients in proportions dictated by certain rather critical specifications. More particularly, these specifications relate to the following:

(1) Synthetic acid soap concentration as indicated by the equivalent carboxyl saponification value of the blend.

(2) Sulfonate concentration as indicated by the organic SO_3 content.

(3) Mutual solvent content.

(4) Water content.

It has been found that the best grade soluble oil should conform to the following specifications:

Equivalent carboxyl saponification value	18–20
Organic SO_3 content	0.45% minimum
Mutual solvent content	0.5% minimum
Water content	2.5–2.75%

In addition to these specifications the soluble oil should be slightly alkaline, for instance containing 0.01–0.10% free NaOH.

When the soap content is equivalent to a carboxyl saponification value of less than about 18, emulsibility usually is not up to the desired standard for highest grade soluble oils; on the other hand, when it exceeds the concentration indicated by a carboxyl saponification value of about 20, there is an increasing tendency for the undiluted soluble oil blend to exhibit heterogeneity or incompatibility of the soaps and hydrocarbon oil. A soap concentration within the range equivalent to 18–20 carboxyl saponification value therefore is preferred, although some variation of these limits is permissible when high quality is not required.

Sulfonates are added to the soluble oil for the purpose of imparting rust-inhibiting characteristics thereto. It has been found that when the soluble oil is used as cutting oil in metal working operations the presence of sulfonates in concentrations specified herein prevents rusting of the metal under service conditions. Sulfonates derived from petroleum lubricating oil fractions by treatment with strong sulfuric acid followed by neutralization with an alkali metal hydroxide as practiced in white oil manufacture have particular utility for the purpose. The percentage of organic SO_3 affords a convenient means of indicating the proper sulfonate concentration. In order to attain the desired rust-preventive characteristics the sulfonate content should be equivalent to not less than about 0.45% organic SO_3, for instance between 0.45% and 0.60%, when sodium sulfonates resulting from white oil manufacture are used. Larger proportions of sulfonates may be employed, although this usually effects little if any further improvement in quality of the soluble oil; however, since sodium sulfonates themselves are good emulsifying agents, the use of such larger proportions will permit lower concentrations of the synthetic acid soaps than specified above without loss of quality.

A minor proportion of a mutual solvent (i. e. a solvent for both oil and water) is added to ensure compatibility of the blended constituents, to reduce viscosity of the blend and to aid emulsibility. Butyl Cellosolve is preferred as the mutual solvent, although various other solvents such as isopropyl alcohol and other alcohols and alcohol-esters may be used. It is desirable to have at least 0.5% mutual solvent in the soluble oil blend but more than 1.0% is seldom if ever required.

The water content of the final blend should lie within a rather narrow range for best results, preferably within the range of 2.5–2.75%, although a range of 2.25–3.0% is permissible. Below 2.25% there is a tendency for gelation to occur, while above 3.0% there is danger of reaching a state of incompatibility of soaps and oil. Usually the water content is adjusted before addition of the mutual solvent in order to prevent loss of the latter.

While the addition of minor amounts of sulfonates, a mutual solvent and water are essential to the attainment, in the highest degree, of the qualities desirable in the finished soluble oil, it will be understood that their addition to such oils is known in the art and such addition is not included in the appended claims, which are confined to the process of producing the soluble oil to which said special ingredients are added.

The viscosity of the lubricating oil used in compounding with these other ingredients to produce a finished soluble oil product is of relatively minor

importance. A light lubricating oil, for instance one having a viscosity of 100 seconds S. U. at 100° F., is preferred in order that the viscosity of the product will not be excessive.

Soluble oils prepared in the above described manner are compatible with soluble oils made from natural naphthenic acids and may be blended therewith in any proportion. In some cases this may result in a blend of higher quality in certain respects than either blend alone. Furthermore, refined synthetic acids obtained from the purifying procedure described above may be blended with natural naphthenic acids and the blend then compounded with the other specified ingredients to produce soluble oil, the only desirable alteration in the soluble oil formula then being a slight reduction in the optimum water content.

Considerable latitude is permissible in the choice of equipment suitable for practicing the present invention commercially. As previously stated, the process may be operated in a continuous manner, in which case the equipment would be designed accordingly; however it is preferable to operate batchwise since simple conventional types of commercial equipment then may be employed. Although the process comprises numerous steps, only two major pieces of commercial equipment are needed in order to carry out all of these in batch operation; specifically, there is required an autoclave for the oxidation step and one conventional type agitator for all the other steps including the final steps of saponifying the synthetic stock and compounding the soluble oil. The autoclave should be constructed of material resistant to the corrosive action of the oxidation products and should be designed so as to withstand the desired pressure. It should be provided with an air inlet line at the bottom and a vent gas line at the top, and with suitable valves for regulating the gas flow and maintaining the desired pressure. It also should be provided with a means for intimately mixing the air and the charge stock, a particularly suitable means being a motor driven impeller or turbine-type stirrer. In addition, since the oxidation reaction is highly exothermic, a cooling coil or other suitable means should be provided for absorbing the heat of reaction and maintaining the temperature at the desired level. Also some means for heating the charge stock to the desired reaction temperature before starting the oxidation should be provided, for instance a steam coil. For carrying out the other steps of the process a conventional cone-bottom type agitator, having sufficient heating coils for maintaining the desired temperature and provided with means for effecting agitation such as an air supply line for blowing, is suitable.

The following example will serve to show how the present invention may be carried out in commercial practice:

Twenty barrels of a 270 S. U. viscosity white oil, obtained by treatment of a Gulf Coastal distillate fraction with fuming sulfuric acid and composed of 1% aromatic rings, 59% naphthene rings and 40% paraffinic chains as determined by Watermann analysis, were charged to a 60 barrel autoclave of the indicated design. Twenty-one barrels of the unsaponifiable portion of oxidation product derived from a previous operation were added to the autoclave and mixed with the fresh charge stock. The mixture was heated until a temperature of approximately 140° C. was reached, whereupon air was injected into the mixture while intimate agitation was being effected by means of an impeller-type mixer. A pressure of 50 pounds per square inch gauge was maintained within the autoclave, with air being supplied at the rate of about 520 cubic feet per minute (measured at atmospheric pressure) and vent gases being withdrawn at the approximate rate of 420 cubic feet per minute. Temperature was maintained at approximately 140° C. throughout the oxidation by means of cooling water circulated through a coil. After approximately eight hours the oxidation was discontinued. The oxidized material comprised approximately 41 barrels having saponification and acid values of 114.5 and 54.3, respectively. This material was pumped from the autoclave into an open-top agitator of approximately 200 barrels capacity and there allowed to cool to 80° C. 4.2 barrels of 50° Bé. caustic soda solution and approximately the same amount of water were added, and the mixture was agitated by blowing with air, the temperature being maintained at about 80° C. by means of a steam coil. Agitation was continued for three hours, during which time water occasionally was added to compensate for that lost through evaporation and thus maintain fluidity. This treatment effected complete saponification of the neutralizable oxidation products and yielded 49.3 barrels of a substantially homogeneous mixture comprising water, soaps, oil and unsaponifiable oxidation products. One hundred and twenty-three barrels of water were added and, after a short period of agitation, the resulting mixture was settled at approximately 80° C. for one-half hour. An upper layer comprising 21 barrels of oil and water-insoluble unsaponifiable oxidation products and a lower layer comprising 151.3 barrels of soap solution were obtained. The upper layer was pumped off through a swing line and used as recycle stock in a subsequent oxidation. To the soap layer was added 21 barrels of a light lubricating oil having a viscosity of 100 seconds S. U. at 100° F. and 1.08 barrels of 95% sulfuric acid calculated to be sufficient for acidifying 50 per cent of the soaps. The mixture was thoroughly agitated and then permitted to stand for two hours at approximately 80° C., whereby an upper layer comprising 37 barrels of oil-synthetic acids mixture and a lower layer comprising 136 barrels of an aqueous solution of soaps of relatively strong acids and sodium sulfate were obtained. The aqueous layer was drawn off and discarded. The upper layer was agitated with 37 barrels of water and then allowed to settle for two hours at about 80° C. The resulting aqueous layer again was drawn off and discarded. The upper layer contained a small amount of entrained water which was removed by air blowing. Thirty-five barrels of refined stock having saponification and acid values of 49.4 and 30.2, respectively, thereby was obtained.

The refined stock was saponified with 1.6 barrels of 50° Bé. aqueous caustic soda, this amount being sufficient to provide a slight excess of alkali. Saponification was accomplished by blowing the mixture of refined stock and alkali at 80° C. for about one-half hour. To the saponified stock 47.2 barrels of light lubricating oil similar to that described above, 5 barrels of crude petroleum sulfonates (mixture of lubricating oil and sodium sulfonates) containing 7.4% organic SO_3, and 1.7 barrels of water were added, and the resulting mixture was blown with air until substantially homogeneous. 0.5 barrel of butyl Cellosolve then was added and the mixture again blown for a short time, whereupon a finished

soluble oil product meeting the following specifications was obtained:

Equivalent carboxyl saponification value		19
Organic SO_3	per cent	0.46
Butyl Cellosolve	do	0.5
Water	do	2.6
Free NaOH	do	0.08

This product was found to conform to highest standards for cutting oils in laboratory tests and under actual service conditions.

We claim:

1. The process of producing soluble oil from petroleum hydrocarbon starting material having lubricating oil consistency and containing naphthenic constituents in amount providing an average of at least one naphthenic ring per molecule and aromatic constituents in amount insufficient substantially to inhibit oxidation, which comprises subjecting said starting material to liquid phase partial oxidation by means of a free-oxygen containing gas at a temperature within the range of 120–165° C. and at a superatmospheric pressure not in excess of 175 pounds per square inch, the conditions of temperature and pressure being such as to effect a commercially practical rate of oxidation but said temperature being sufficiently low to prevent the formation of sludge-like products, continuing the oxidation until the oxidized mixture contains a substantial proportion of synthetic acids suitable for soluble oil manufacture while avoiding the formation of more highly oxidized acidic products in appreciably detrimental proportion, treating the oxidized mixture with an aqueous solution of alkali metal hydroxide under such conditions as to effect complete saponification and yield an aqueous mixture comprising alkali metal soaps, unsaponifiable oxidation products and unoxidized hydrocarbons, fractionally acidifying said aqueous mixture with a mineral acid in amount sufficient to convert to free acids a predominant proportion of the soaps of relatively weak acids having utility in manufacture of high quality soluble oil but insufficient to acidify a substantial proportion of the soaps of relatively strong acids having characteristics detrimental to high quality soluble oils, separating resulting aqueous and oily phases, washing the oily phase with water to remove water-soluble contaminants therefrom and thereby yield a refined synthetic acid product the acidic constituents of which include no substantial proportion of relatively strong acids, saponifying said product with an alkali metal hydroxide and blending the saponified product with petroleum oil to yield, as the desired final product, a blend capable of forming stable oil-in-water emulsions.

2. The process of producing soluble oil from petroleum hydrocarbon starting material having lubricating oil consistency and containing naphthenic constituents in amount providing an average of at least one naphthenic ring per molecule and aromatic constituents in amount insufficient substantially to inhibit oxidation which comprises blending said starting material with the recycle stock hereinafter specified, subjecting the blend to liquid phase partial oxidation by means of a free-oxygen containing gas at a temperature within the range of 120–165° C. and at a superatmospheric pressure not in excess of 175 pounds per square inch, the conditions of temperature and pressure being such as to effect a commercially practical rate of oxidation but said temperature being sufficiently low to prevent the formation of sludge-like products, continuing the oxidation until the oxidized mixture contains a substantial proportion of synthetic acids suitable for soluble oil manufacture while avoiding the formation of more highly oxidized acidic products in appreciably detrimental proportion, treating the oxidized mixture with an alkali metal hydroxide under such conditions as to effect complete saponification, diluting the saponified mixture with water, separating from the diluted mixture an oily phase comprising unsaponifiable material suitable for use as recycle stock in a subsequent oxidation, fractionally acidifying the remaining aqueous layer with a mineral acid in amount sufficient to convert to free acids a predominant proportion of the soaps of relatively weak acids having utility in manufacture of high quality soluble oil but insufficient to acidify a substantial proportion of the soaps of relatively strong acids having characteristics detrimental to high quality soluble oils, separating resulting aqueous and oily phases, washing the oily phase with water to remove water-soluble contaminants therefrom and thereby yield a refined synthetic acid product the acidic constituents of which include no substantial proportion of relatively strong acids, saponifying said product with an alkali metal hydroxide and blending the saponified product with petroleum oil to yield, as the desired final product, a blend capable of forming stable oil-in-water emulsions.

3. The process as defined in claim 2 wherein lubricating oil is added to the aqueous soap layer before subjecting said layer to fractional acidification.

4. A soluble oil capable of forming stable oil-in-water emulsions which comprises a major proportion of lubricating oil, alkali metal soaps of relatively weak synthetic acids having characteristics suitable for manufacture of high quality soluble oil in concentration equivalent to a carboxyl saponification value of 18–20 mgs. KOH per gram, alkali metal sulfonates in concentration at least sufficient to cause said soluble oil to have an organic SO_3 content of 0.45 per cent, at least 0.5 per cent of an effective mutual solvent, 2.25–3.00 per cent water and a small percentage of free alkali, said weak synthetic acids having been derived, so as to exclude the presence therein of any substantial proportion of relatively strong synthetic acids detrimental to high quality soluble oil, from the reaction mixture obtained by liquid phase partial oxidation of a petroleum lubricating oil fraction containing a substantial proportion of naphthenic constituents under oxidizing conditions preventing the formation of sludge-like products.

5. The process of producing high quality soluble oil from petroleum lubricating oil containing an average of at least one naphthene ring per molecule and aromatic constituents in amount insufficient substantially to inhibit oxidation, which comprises oxidizing said starting material in liquid phase by means of a free-oxygen containing gas at a temperature within the range of 120–165° C. and at a superatmospheric pressure not in excess of 175 pounds per square inch, discontinuing the oxidation when the reaction mixture has a saponification value on the order of 110–120 milligrams KOH per gram, completely saponifying the reaction mixture with an aqueous solution of alkali metal hydroxide thereby to form an aqueous mixture comprising alkali metal soaps, unsaponifiable oxidation products and unoxidized hydrocarbons, fractionally acidi-

fying said aqueous mixture with a mineral acid in amount required to acidify on the order of 50 per cent of the alkali metal soaps thereby liberating relatively weak acids having utility in manufacture of high quality soluble oil, separating resulting aqueous and oily phases, washing the oily phase with water to remove water-soluble contaminants therefrom and yield a refined synthetic acid product the acidic constituents of which include no substantial proportion of relatively strong acids detrimental to high quality soluble oil, saponifying said product with an alkali metal hydroxide and blending the saponified product with petroleum oil to yield, as the desired final product, a blend capable of forming stable oil-in-water emulsions.

6. The process according to claim 5 wherein the said starting material is a naphthenic base lubricating oil having a S. U. viscosity of about 150–350 seconds at 100° F.

7. The process of producing high quality soluble oil from petroleum lubricating oil containing an average of at least one naphthene ring per molecule and aromatic constituents in amount insufficient substantially to inhibit oxidation, which comprises oxidizing said starting material in liquid phase by means of a free-oxygen containing gas at a temperature within the range of 120–165° C. and at a superatmospheric pressure not in excess of 175 pounds per square inch, discontinuing the oxidation when the reaction mixture has a saponification value on the order of 110–120 milligrams KOH per gram, completely saponifying the reaction mixture with an aqueous solution of alkali metal hydroxide, diluting the saponified mixture with water, separating from the diluted mixture an oily phase comprising unsaponifiable material suitable for use as recycle stock in a subsequent oxidation, fractionally acidifying the remaining aqueous layer with a mineral acid in amount required to acidify on the order of 50 per cent of the alkali metal soaps thereby liberating relatively weak acids having utility in manufacture of high quality soluble oil, separating resulting aqueous and oily phases, washing the oily phase with water to remove water-soluble contaminants therefrom and yield a refined synthetic acid product the acidic constituents of which include no substantial proportion of relatively strong acids detrimental to high quality soluble oil, saponifying said product with an alkali metal hydroxide and blending the saponified product with petroleum oil to yield, as the desired final product, a blend capable of forming stable oil-in-water emulsions.

8. The process according to claim 7 wherein the said starting material is a naphthenic base lubricating oil having a S. U. viscosity of 150–350 seconds at 100° F.

9. A soluble oil capable of forming stable oil-in-water emulsions which comprises a major proportion of lubricating oil and a minor proportion of alkali metal soaps of relatively weak synthetic acids possessing the characteristics of the acid fraction obtained by oxidizing a naphthenic base lubricating oil of about 270 S. U. viscosity at 100° F. in liquid phase by means of a free-oxygen containing gas at a temperature within the range of 120–165° C. and a superatmospheric pressure below 175 pounds per square inch, discontinuing the oxidation when the reaction mixture has a saponification value of 110–120 milligrams KOH per gram, completely saponifying the reaction mixture with an alkali metal hydroxide, fractionally acidifying about 50 per cent of the soaps in the saponified mixture to obtain a relatively weak acid fraction and washing said fraction with water.

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