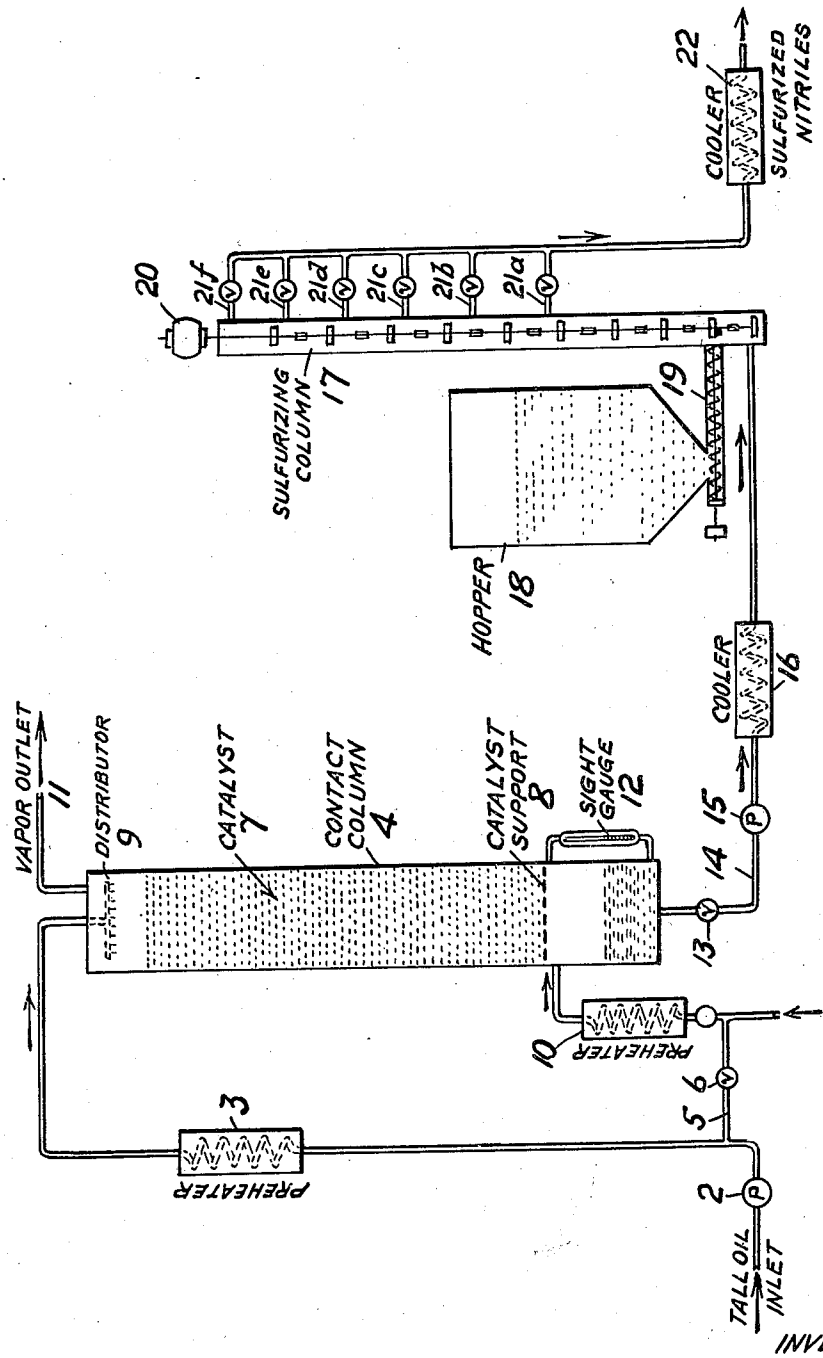
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LUBRICANT

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LUBRICANTS

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The object of my invention is to provide special sulfurized lubricants for use in severe service, such, for example, as non-emulsifiable mild extreme pressure lubricants, emulsified cutting oils and greases; also special sulfurized lubricants which are non-corrosive to such non-ferrous metals as brass, copper, bronze and aluminum.

My invention comprises a mineral oil stock to which has been added a minor proportion of oil-soluble sulfurized nitriles which have been formed by the hereinafter described method of reacting sulfur with nitriles of certain selected organic acids.

Sulfurized esters or glycerides of fatty acids have been used in various special lubricants. However, lubricants which contain esters or glycerides may undergo hydrolysis or become rancid, thereby developing an acidity which imparts corrosive properties to the lubricant. Hydrolysis is also objectionable for the reason that many lubricants, particularly soluble oils and greases, for best performance, should be slightly alkaline. Sulfurized nitriles, on the other hand, do not undergo hydrolysis under conditions encountered in service and therefore are of particular utility in the manufacture of special lubricants. The preparation of such sulfurized nitriles soluble in, and suitable as additives to, lubricants, presents, however, serious problems which I have succeeded in solving. A full disclosure of my invention therefore necessitates a detailed description of the method by which sulfurized nitriles, suitable for use as additions to lubricants and for imparting to lubricants the qualities which it is desired they shall have, should be prepared; and the following description is therefore mainly addressed to such method. I should here state that it should be understood that I do not claim to be the first to, in any manner, react fatty acid nitriles with sulfur or sulfur compounds, or to be the first to add such reacted nitriles to lubricants to produce extreme pressure lubricants. Thus, Ralston U. S. Patents 2,125,853 and 2,141,142 disclose the preparation of reaction products of nitriles with sulfur monochloride or with sulfur monochloride and sulfur and their use in extreme pressure lubricants. These products, however, contain sulfur and chlorine in chemical combination. It is a characteristic feature of my improved lubricant that it contains combined sulfur but is free of chlorine or combined chlorine.

My method of producing such an improved sulfurized nitrile involves its preparation from starting materials containing higher molecular weight organic acids, such as fatty acids and rosin acids, in two major steps comprising conversion of the acids to nitriles and the sulfurization of the nitriles.

Numerous methods of converting fatty acids into nitriles are known, some of which are of only academic interest while others have shown commercial value. In the latter methods the conversion generally has been effected by causing the fatty acids and ammonia to react in either liquid or vapor phase according to the following reactions:

(1) $RCOOH+NH_3 \rightarrow RCOONH_4$

(2) $RCOONH_4 \rightarrow RCONH_2+H_2O$

(3) $RCONH_2 \rightarrow RCN+H_2O$

Ralston et al. U. S. Patent 2,061,314 discloses a method of effecting these reactions in liquid phase, and Potts et al. U. S. Patent 2,314,894 discloses an improved method comprising both liquid and vapor phase reactions. Methods wherein these reactions have been carried out wholly in vapor phase in many cases have proved unsatisfactory due to decomposition of the fatty acids on vaporization. Such of the known methods as prevent decomposition of the fatty acids on vaporization and are otherwise of commercial value may be used, with some starting materials, to form nitriles that may be subjected to the sulfurizing step of my process. However, with certain preferred starting material, these methods are not altogether satisfactory, as is more fully explained hereinafter; and my process preferably involves, as a first major step, an improved method for converting organic acids to nitriles which, when sulfurized in accordance with the second step of my process, will produce a sulfurized nitrile whose addition to lubricating oils or greases will reliably impart to them the qualities sought.

As starting materials for conversion to nitriles I may utilize such materials as stearic acid, oleic acid, lard oil acids and other fatty acids of animal, vegetable or marine origin which have at least ten carbon atoms. I have found that tall-

oil, which is a mixture of fatty and rosin acids obtained as a by-product in paper manufacture from pine and other non-deciduous woods, is particularly advantageous as a starting material and is also preferred because of its ready availability and low cost. However, whether starting with talloil, or any other organic acid having at least 10 carbon atoms and selected from the group consisting of fatty acids and rosin acids, I first form nitriles under conditions such that no substantial amount of reaction products boiling above the boiling range of the starting acids are formed, and then react the so-formed nitriles with free sulfur at an elevated temperature for a length of time sufficient to give a homogeneous product but insufficient to cause the formation of mineral oil-insoluble products. I have discovered that nitriles which are higher boiling than the starting acids from which they were prepared, apparently due to polymerization during their formation, on sulfurizing yield products which are substantially oil-insoluble and therefore unsuitable in the present application. Further, I have discovered that nitriles, even though they may be of suitable boiling range, likewise yield substantially oil-insoluble products on sulfurization unless the reaction between the nitriles and sulfur is carried out in relatively short time.

When such starting materials as stearic acid, oleic acid or lard oil acids are used, various heretofore known methods of preparing the nitriles are suitable, as hereinbefore stated. However, when, as is preferred, talloil is used as the starting material, these known methods generally give a product containing a considerable proportion of nitriles which boil higher than the boiling range of the talloil and which on sulfurization form undesirable oil-insoluble products. In order to use nitriles prepared from talloil according to methods heretofore known, it usually is necessary to remove the high boiling material, for instance by distillation, thus sacrificing yield of nitriles in order to obtain the desired quality. I have discovered that nitriles of suitable boiling range may be prepared from talloil in accordance with the reactions listed above by contacting the talloil in liquid phase and at elevated temperature with ammonia vapor under such conditions that the time of contact is relatively short, for instance not more than say twenty minutes and preferably less if possible. This causes the desired reactions to proceed without allowing the reactions that result in the formation of high boiling nitriles to take place to a substantial extent. In order to obtain the desired high yield in such short time of contact it obviously is requisite that very intimate contact between the talloil and ammonia vapor be effected, and it has been found that a packed column provides a particularly suitable means of effecting an intimate but short-timed contact. Further, it is desirable to carry out the reaction in the presence of a dehydrating catalyst such as alumina or silica gel in order to accelerate the reaction, and a preferable means of accomplishing this is by employing catalyst as the packing material for the contact column. Thus my preferred method of preparing nitriles comprises continuously feeding heated talloil to the top of a contact column packed with a dehydrating catalyst, continuously passing ammonia vapor through the column and allowing the talloil to trickle over the catalyst and flow by gravity to the base of the column, thereby effecting an intimate contact of short duration between the liquid and vapor phases.

The optimum temperature range for carrying out the contact operation between talloil and ammonia vapor has been found to be about 325–375° C., this giving the maximum yield of nitriles of suitable boiling range. Temperatures below 325° C. tend to cause decreased rate of reaction, thus requiring a longer time of contact with a resultant increase in the proportion of undesirable high-boiling material formed. Temperatures above 375° C. tend to cause decreased yield of desirable nitriles, possibly by causing cracking of the reaction products, cracking of the talloil itself and perhaps an unfavorable displacement in the equilibrium of the first step of reaction illustrated by Equation 1, supra.

Sulfurization of the nitriles is accomplished by reacting elemental sulfur with the nitriles and may be carried out in either batch or continuous manner. There are two critical, interrelated factors involved in this step, namely, the reaction temperature and the time of reaction. In order to initiate the reaction between nitriles and sulfur the temperature should not be much below 190° C. This minimum temperature is rather critical. Thus a temperature of 180° C., while not greatly below 190° C., gives an exceedingly slow rate of reaction. A product produced by a slow rate of reaction contains insoluble material varying from small to large amounts dependent upon the reaction time; and filtered oil, blended with such a product, even though the amount of insoluble material contained therein may be comparatively small, precipitates, after a few days of aging, a black sludge, as hereinafter fully explained. The product that I produce should contain no more than a trace of insoluble material. This requires, in the sulfurizing step as above stated, a short time of reaction, and this short time of reaction in turn requires a minimum temperature which more nearly approaches 190° C. than 180° C. and therefore is not substantially below 190° C. After the reaction has been initiated by raising the temperature of a mixture of nitriles and sulfur to 190° C., there is a tendency toward further increase in temperature due to the exothermic nature of the reaction. This is not objectionable provided the processing equipment is properly designed for handling the materials at higher temperature with safety, and provided, of course, that the temperature is not allowed to rise so high as to effect any substantial cracking of the nitriles. The necessary temperature factor is, therefore, highly flexible so far as concerns its upper limit, but critical in that it is necessary that it should be within a zone having the specified lower limit. Operation under such a temperature allows the reaction to proceed only so long as to give a product that will be homogeneous at ordinary temperatures, but not so long as to cause formation of oil-insoluble products. The time of reaction also depends on the proportion of sulfur used. The lower the proportion of sulfur and the higher the reaction temperature, the shorter is the required reaction time. At a temperature of about 190–200° C., it is desirable that the reaction time be not over about 15 minutes, although somewhat longer reaction times may not be too unsatisfactory for practical operation.

In the accompanying single sheet of drawing there is shown schematically a preferred form of apparatus for practicing the above described process, which, for purposes of illustration, is described in connection with the processing of talloil, but which is also suitable for the processing

of other charge stocks such as stearic acid, oleic acid and lard oil acids.

As shown in the drawing, talloil, which may be either crude or refined and which usually will conform to the following specifications:

Saponification No		170–185
Acid No		160–180
Iodine No		90–130
Fatty acids	per cent	44–60
Rosin acids, calculated as abietic acid	do	34–47
Sterols, higher alcohols, hydrocarbons, etc	do	6–10
Moisture	do	0.1–0.3
Ash	do	0.1

is charged to the appartus by means of charge pump 2. The talloil passes through preheater 3, where its temperature is raised to 325–375° C., and into contact column 4. It has been found that talloil at such elevated temperature has a tendency to decompose when not in the presence of ammonia, and in order to prevent such decomposition it is desirable that the time interval between entrance of the oil to preheater 3 and its entrance into contact column 4 be short. It also is desirable to add a small proportion of ammonia to the talloil before preheating as further insurance against decomposition, and line 5 containing valve 6 is provided for this purpose. Contact column 4 is packed with a granular dehydrating catalyst 7 such as alumina, the catalyst being supported at a point above the bottom of the column by a suitable catalyst support 8 such as a wire grille. The entering talloil preferably is distributed evenly on the alumina near the top of contact column 4 by means of a distributor 9 which may be of any suitable form. Ammonia vapor, preferably anhydrous, is preheated to a temperature of 325–375° C. in preheater 10 and is passed into the column suitably at a point just below catalyst support 8. The talloil flows down the column as a thin film on the surfaces of the catalyst and countercurrently to the ascending ammonia vapor stream, thereby intimately commingling with the ammonia. At the top of contact column 4 there is provided vapor outlet line 11 through which effluent vapors, comprising excess ammonia, water formed in the reaction and any low boiling organic materials present or formed during the reaction, are withdrawn. These vapors preferably are passed through apparatus for separately recovering ammonia and any low boiling organic materials, which is not shown in the drawing since apparatus suitable for accomplishing this is well known and forms no part of the present invention. The liquid stream flows by gravity from the catalyst zone and collects in the base of the column, and sight gauge 12 is provided as an aid in maintaining a low liquid level therein. The liquid level is regulated by means of valve 13 in outlet line 14 or by varying the speed of pump 15. The reaction product which is withdrawn from the base of the column by means of pump 15 consists predominately of nitriles having a boiling range not higher than that of the talloil charge stock, provided the contact column is of suitable height and proper operating conditions are maintained.

Contact column 4 obviously should be insulated or provided with suitable heating means for maintaining a temperature of 325–375° C.

On continued operation the catalyst 7 in contact column 4 usually will decrease in activity due to deposition of small amounts of gums, resins or polymerized materials. Regeneration of the catalyst may be accomplished, when desired, by washing with a suitable solvent, for instance, benzene.

The nitrile product withdrawn from contact column 4 flows through cooler 16 where its temperature is reduced preferably to a level such that the temperature within sulfurizing column 17 will be about 190–200° C., whence it passes to the base of sulfurizing column 17. Sulfur also is added near the base of the column in proportion desired for reaction with the nitriles. As illustrated in the drawing, this may be done by feeding finely divided sulfur from hopper 18 to the column by means of screw conveyor 19. Sulfurizing column 17 is provided with a stirrer driven by electric motor 20 and comprising a centrally located shaft along which is attached in suitable space arrangement a plurality of blades or other means for dispersing the sulfur and effecting intimate contact between the nitriles and sulfur as the mixture flows up the column. It is desirable that sulfurizing column 17 be of sufficiently small diameter so that the mixing effected by the stirrer is mainly lateral without a substantial amount of vertical mixing in order that a reasonably definite continuous flow of the mixture up the column obtains. Sulfurizing column 17 also is provided with a plurality of outlet lines (21—*a*, *b*, *c*, *d*, *e*, *f*) vertically spaced along its upper section, all provided with valves by means of which the level of withdrawal of reaction products is controlled. With this arrangement the time of reaction between the nitriles and sulfur depends on the rate of flow, the diameter of the sulfurizing column and the level from which the reaction mixture is withdrawn; thus for a given rate of charge to the process the reaction time may be varied as desired by varying the level of withdrawal. In order to maintain the desired short reaction time for various rates of flow, one of the lower levels, for instance line (21—*a*), would be used for a slow rate of flow while a higher level, for instance line (21—*e*), would be used for a faster rate. Obviously the equipment must be properly designed to allow suitable adjustment for any charge rate that may be employed.

The sulfurized nitriles from column 17 flow through cooler 22 and thence may be sent to storage or directly to a blending tank as base stock for compounding my improved special lubricant.

In the step of preparing nitriles from talloil, the importance of a short time of contact as effected in the process described above is illustrated by the following comparison between the present method and a known method comprising prolonged batch treatment of liquid talloil with ammonia vapor:

	Known method (prolonged batch treatment)	Present method (short-timed countercurrent treatment)
Reaction temperature	260–290° C.	340–375° C.
Approximate time of contact	6 hrs.	10 min.
Acid number of talloil charge	175	175.
Acid number of product	5.5	4.7.
Per cent. of product having suitable boiling range.	55	92.
Yield of nitriles of suitable boiling range, calc'd. as per cent. of maximum possible yield.	52	89.

As indicated by the acid numbers of the products,

approximately the same proportion of the charge was converted to nitriles in each case. However, with the known method only 55 per cent. of the product was of suitable boiling range (i. e. not higher than the boiling range of the talloil), whereas 92 per cent. of the product prepared according to my improved method was of suitable boiling range. Thus the latter product contained only 8 per cent. of nitriles of higher boiling range—an amount insufficient to cause the product on sulfurization to yield oil-insoluble material—while the product of the known method contained 45 per cent. of such higher boiling nitriles which rendered it unsuitable for preparation of sulfurized products for addition to lubricants.

In the step of sulfurizing the nitriles, the importance of a short reaction time may be demonstrated by sulfurizing samples of the nitriles for various lengths of time, mixing the sulfurized samples with mineral oil and noting the amounts of insoluble material, filtering the blends to remove the insoluble material, then allowing the filtered blends to age at a low temperature and noting any further formation of insoluble material. The data given below are illustrative of experiments of this type which have been made with nitriles prepared from talloil according to the method described above. In each of these experiments 25 parts of sulfur were reacted with 75 parts of nitriles at a temperature of 190–200° C., and 10 parts of the resulting sulfurized nitriles were blended with 90 parts of mineral oil.

Reaction time, minutes	Amount of insoluble material in unfiltered blend	Observations on filtered blend after aging at 6° C.
5	Trace	No separation after 30 days of aging.
35	Small amount	Precipitate after 6 days of aging; black sludge after 8 days of aging.
65	Considerable amount	Precipitate after 3 days of aging; black sludge after 7 days of aging.

This tabulation indicates that a reaction time less than 35 minutes is required in order to produce stable products.

A preferable sulfur content for the sulfurized nitriles is 20–25%, although it is not difficult to incorporate somewhat higher percentages of sulfur in the nitriles. The amount of base stock that should be blended with the lubricant will, of course, vary with different lubricants and with different uses for which the lubricant is intended. As an example, in preparing moderately extreme pressure lubricants, the base stock may be blended with mineral oil of suitable viscosity and flash point in the proportion of about 10 parts of base stock to 90 parts of oil.

While the invention herein claimed is a lubricant containing a major proportion of mineral oil and a minor proportion of oil soluble sulfurized nitriles resultant from the use of the process, and variations thereof, hereinbefore described, it will be understood that these sulfurized nitriles may find other useful applications and therefore such sulfurized nitriles and the process of producing them are separately claimed in a separate application, filed June 25, 1943, Ser. No. 492,227, of which this application is a division.

What I claim and desire to protect by Letters Patent is:

1. A lubricant comprising a major proportion of mineral oil and a minor proportion of oil-soluble sulfurized nitriles free of combined chlorine and formed by reacting sulfur at a temperature not substantially less than 190° C. and under substantially non-polymerizing conditions with nitriles of organic acids having at least 10 carbon atoms and selected from the group consisting of fatty acids and rosin acids, said lubricant being characterized by stability against settlement of sludge after a comparatively long period of aging.

2. A lubricant comprising a major proportion of mineral oil and a minor proportion of oil-soluble sulfurized nitriles free of combined chlorine and formed by reacting sulfur with nitriles of talloil at a temperature not substantially less than 190° C. and under substantially non-polymerizing conditions, said lubricant being characterized by stability against settlement of sludge after a comparatively long period of aging.

3. A lubricant comprising a major proportion of mineral oil and a minor proportion of oil-soluble sulfurized nitriles free of combined chlorine and formed by reacting sulfur at a temperature not substantially less than 190° C. and under substantially non-polymerizing conditions with nitriles of organic acids having at least 10 carbon atoms and selected from the group consisting of fatty acids and rosin acids and no substantial proportion of which boils above the end boiling point of such acids, said lubricant being characterized by stability against settlement of sludge after a comparatively long period of aging.

4. A lubricant comprising a major proportion of mineral oil and a minor proportion of oil-soluble sulfurized nitriles free of combined chlorine and formed by reacting sulfur, at a temperature not less than 190° C. and under substantially non-polymerizing conditions, with nitriles of talloil no substantial proportion of which boils above the end point of talloil, said lubricant being characterized by stability against settlement of sludge after a comparatively long period of aging.

SAMUEL EDWARD JOLLY.