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PROCESS OF MAKING SULFURIZED JOJOBA OIL

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1 Claim. (Cl. 260—399)

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This invention relates to sulfur-bearing compositions prepared by sulfurizing the oil of the jojoba bean which is the seed of the *Simmondsia californica* of the family Buxaceae found in Arizona, California and the western parts of Mexico.

An object of this invention is to prepare a sulfur bearing composition for use as a lubricant or extreme pressure additive from sulfurized jojoba bean oil, which is an unsaturated liquid vegetable wax. Another object is to provide lubricating compositions of high sulfur content. Still another object is to prepare light-colored compositions of high sulfur content from which the sulfur does not precipitate. Other objects will be apparent from the description which follows.

Up to the present time, although most of the known oils have been sulfurized, lard oil and sperm oil appear to be most widely and successfully used for the preparation of sulfur-bearing lubricants and extreme pressure additives. Sperm oil is claimed by many to be superior to lard oil for this use. Sperm oil is composed largely of a mixture of true liquid waxes possessing unsaturation in both its acidic and alcoholic components, and, although the C_{18} chain predominates, other chains are also present so that the average chain is between 17 and 18 carbon atoms in length. Also present are minor proportions of stearines. Jojoba oil is also a true liquid wax possessing unsaturation in both its acidic and alcoholic components. However, the proportion of chains possessing 18 or less carbon atoms is so small as to the negligible. Its acidic component is comprised almost entirely of C_{20} and C_{22} chains in such a ratio that the average acidic chain is between 20 and 21 carbon atoms in length. Its alcoholic portion consists entirely of C_{20} and C_{22} chains in such a ratio that the average chain is between 21 and 22 carbon atoms in length. The iodine number of jojoba bean oil is about the same as that of sperm oil.

Roughly, then, jojoba bean oil would appear to be a substantial equivalent of the major portion of sperm oil were it not for two unobvious and unexpected properties which are pointed out later.

Jojoba bean oil possesses several obvious advantages over sperm oil:

1. Its slight but pleasant odor is a distinct advantage over the unmistakably fishy odor of sperm oil.

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2. Crude jojoba oil contains no stearines and very little besides the liquid wax, so that the crude oil needs little or no treatment to prepare it for most industrial purposes.

3. It is a native of North America and is a vegetable product, so that its production can be carefully controlled and does not depend on the vagaries of nature to the same extent as does the production of sperm oil.

Jojoba bean oil, however, possesses certain advantages which are not obvious. It will take up a much larger amount of sulfur than will sperm or lard oils. A study of the characteristics and properties of jojoba oil and sperm oil shows that the average molecular weight of jojoba oil is roughly 18% greater than that of sperm oil. Under such conditions, stoichiometric ratios would suggest that jojoba oil can not combine with as much sulfur as it is possible for sperm oil to do. On the other hand, the iodine numbers of sperm and jojoba oils being very similar, it could be assumed that both oils would take up about the same amounts of sulfur. On sulfurization, however, entirely unexpected results were obtained. It was found that jojoba oil takes up about 25% more sulfur than sperm or lard oils do. As has been already pointed out, there is no way of predicting this novel behavior of jojoba oil which places it in a separate and unique position among the natural oils.

Another unpredictable advantage of jojoba bean oil is that it does not darken to the same extent as other oils on sulfurization. Past experience has shown that the larger the proportion of sulfur added to a fat or oil, the darker the color of the resultant sulfur-bearing product. Jojoba oil takes up more sulfur than does sperm or lard oil and yet the color of this highly sulfurized jojoba bean oil is much lighter than that of the less highly sulfurized sperm and lard oils. Herein lies a second unique, unexpected, the unpredictable advantage of jojoba oil, which, when sulfurized to the point of carrying at least 25% more sulfur than is possible with such oils as sperm or lard has a lighter color than the sulfurized products of the latter oils. One would be led to expect highly sulfurized jojoba bean oil to be black or nearly so

in view of the extremely dark brown color of sulfurized sperm and lard oils.

A third unexpected advantage of jojoba oil is its ability to remain liquid when highly sulfurized, whereas sperm oil requires mineral oil to keep it liquid.

The usual method of sulfurizing oils such as sperm or lard is to heat them with the desired amount of sulfur for a long time at 360° F. to 400° F.; for example, for 3 to 4 hours at about 380° F. I have found that sulfurization occurs rapidly provided the temperature is high enough, and that long heating is not necessary. With good agitation the reaction begins at about 300° F. and is exothermic. In view of this my method consists in heating the oil and adding the sulfur gradually; for example, adding the first portion at about 250° F. while agitating it. The rest of the sulfur is added portionwise as the temperature rises, adding the last of the sulfur at not above 400° F., at which temperature the heating is stopped.

If the oil is sulfurized in the presence of sufficient mineral oil or if the proportion of sulfur is low, the final product is a liquid. If no mineral oil, or a low proportion thereof is present, and the amount of sulfur is near a maximum, the product is not a liquid, but a solid, which, in the case of most vegetable oils, including jojoba oil, and many highly unsaturated mineral oils, is a factice-like material. However, in the case of jojoba bean oil, by a modification of the process I may obtain a liquid product of high sulfur content when mineral oil is in low proportion or is absent. The modification (which is used only when highly sulfurized products are made and when mineral oil is absent or present only in small proportion) consists in keeping the reaction mixture at between about 350° F. and 400° F. for a relatively short time (up to about 20 minutes) before it is allowed to cool for blowing. The temperature may be held at a selected point between 350° and 400° F. for the necessary time or the batch may be allowed to cool to about 350° F. and reheated to about 400° F., the reheats being repeated during the time necessary to obtain a liquid product. Thus, after the temperature has reached its highest, the batch is allowed to cool to about 350° F.–360° F. and held at this temperature for 10–20 minutes, or, it is allowed to cool to 350° F.–360° F. and then reheated to, but not held at 390°–400° F.

When the sulfur composition has cooled to about 250 F., a current of air is blown through it while keeping the temperature at this point. The oil is then allowed to cool. The purpose of blowing with air is to prevent subsequent development of a hydrogen sulfide odor. When blown in this way, hydrogen sulfide rarely develops in a stored oil, whereas unblown oil usually develops a strong odor in 24 to 48 hours.

The following is a specific example of my sulfurization process which is applicable to any vegetable or animal oil, but particularly to joboba bean oil. The oil is heated to about 250° F. and with stirring a quarter of the sulfur is added. When the temperature is raised to 300° F., a second quarter is added; at 350° F. a third; and at 365° F. the fourth quarter of the sulfur is introduced. The temperature is then taken rapidly to 380° F. and heating discontinued. The temperature generally increases some 15° to 25° F. after removal of the heat. The batch is then given the secondary heating described above, in order to insure a liquid product, after which, when the batch has cooled to 250° F., a blast of air is forced through it and this is continued for 2 hours, holding the temperature at 250° F. Heating is then stopped, and when the temperature falls to 150° F., blowing is discontinued.

As stated above, jojoba bean oil forms a factice when treated with large proportions of sulfur, unless it is given the secondary heating after the sulfurization, as described. However, such factice differs from that produced by many animal and vegetable oils in its complete solubility and stability in mineral oil. Rapeseed oil, sunflower seed oil, and menhaden oil are notable examples of oil which produce factices which are, at best, only partially soluble in mineral oil. Crude tall oil produces no factice, but a black tarry mass separates from a solution of the sulfurized oil on standing.

My short-time sulfurization process not only results in a saving of time and fuel but also produces a higher sulfur content of the oil as shown by analysis. A sperm oil heated in the proportion of 70 parts oil, 10 parts 300-sec. mineral oil with 24 parts of sulfur at 375° F. for 3 hours shows only 17% sulfur by analysis as against 21.8% sulfur when the same ingredients were heated by my process.

In the following examples, which are only illustrative and are not to be considered as limiting, there are shown reaction mixtures containing jojoba bean oil and sulfur in varying proportions. Also are shown mixtures containing sperm or lard oils and sulfur for comparison. In place of raw jojoba oil, as expressed or extracted from the beans, I may use refined oils or the saponifiable and unsaponifiable constituents of jojoba oil. Parts are by weight in all examples.

Example 1

	Parts
Jojoba bean oil	144
Sulfur	64

This was treated by adding the sulfur portionwise as previously described. When the temperature fell to 350° F. a portion was removed and the batch reheated to 400° F. Again, when the temperature fell to 350° F., a sample was removed and the batch again heated to 400° F. When the temperature had again fallen to 350° F., a third portion was removed and the remainder of the batch allowed to cool and blown as hereinabove described. The first and second portions which had been removed turned to stiff rubbery solids. The third portion and the batch remained liquid, the major difference between them being the odor of hydrogen sulfide developed in the small portion, whereas the blown base remained free of any odor of sulfide.

The above example shows a liquid sulfurized jojoba bean oil containing a maximum of combined sulfur and prepared in the absence of a mineral oil. It may be stated that sperm oil, when sulfurized with a maximum amount of sulfur in the absence of mineral oil, forms a solid factice no matter whether the heating is continued between 350°–400° F. for a long or short time.

Example 2

	Parts
Sperm oil (38° cold test)	70
300-sec. mineral oil	10
Sulfur	24

These proportions have been found to be satisfactory for yielding a liquid sulfurized sperm oil

containing a maximum of combined sulfur. The oil was heated and the sulfur added gradually, starting at 250° F. and finishing the addition at about 360° F. The temperature was then allowed to rise to 400° F. During a period of about 20 minutes the temperature was allowed to fall to 350° F., then raised to 400° F. Finally, the batch was allowed to cool to 250° F. and blown for 2 hours. The product after cooling was a liquid which analyzed 21.8% sulfur.

Another batch of the same formula was made but was given a long period of heating of 3 hours at 380° F. after the sulfur addition. It was blown as above. The sulfur content of the liquid product was only 17%. (Example 2A.)

It may be remarked that in all cases where the results of sulfur analyses are given, the determination is made after allowing the product to stand for several days to allow any uncombined sulfur to settle out and then filtering.

Example 3

	Parts
Jojoba bean oil	70
300-sec. mineral oil	10
Sulfur	24

The above proportions are the same as in Example 2 and the portion-wise addition of sulfur was likewise employed. When the temperature fell to 350° F., a sample portion was removed and the batch reheated to 400° F. At 350° F. a second portion was removed and the batch then completed as previously described. The first portion removed was a solid while the second portion and the batch (after blowing) were liquid. The sample portion had an odor of hydrogen sulfide while the base did not. The sulfur content analyzed 22.8%.

A batch was also prepared wherein the same ingredients were first sulfurized and then, when the temperature dropped to 350° F., it was held at this temperature 15 minutes before proceeding to finish the batch. Results here duplicated those obtained when reheating was employed as described immediately above. In both cases any small precipitate of sulfur was removed before analysis.

Example 4

	Parts
Jojoba bean oil	60
300-sec. mineral oil	23
Sulfur	21

This resulted in a liquid product without any subsequent heat treatment. There was very little sulfur precipitated from the oil.

Example 5

	Parts
Hydrolyzed jojoba bean oil	70
300-sec. mineral oil	10
Sulfur	24

A liquid product resulted which showed no sulfur precipitation.

Example 6

	Parts
Jojoba saponifiables	70
300-sec. mineral oil	10
Sulfur	24

A liquid product resulted which showed a trace of sulfur precipitation.

Example 7

	Parts
Jojoba unsaponifiables	70
300-sec. mineral oil	10
Sulfur	24

This was a liquid with a slight trace of sulfur precipitation.

Example 8

	Parts
Jojoba oil	66
300-sec. mineral oil	9
Sulfur	29

A sample removed when the temperature had fallen to 350° F. turned solid, but after reheating to 400° F. and allowing to cool, a sample remained liquid. The finished batch was a very viscous liquid which showed a slight sulfur precipitation. It was filtered before analysis. Sulfur content of the vegetable oil of the product was 30.8%, which clearly demonstrates the ability of jojoba oil to take up a much larger proportion of sulfur than is the case with sperm oil.

The sulfurized jojoba oil of this example was made into a 10% solution using a 100-sec. mineral oil as solvent. The sulfurized sperm oil produced in Example 2 was also made into a 10% solution with the same mineral oil and several specifications of the two were determined.

	Jojoba	Sperm
Gravity, ° API	23.5	23.5
SSU vis./100° F.	151	155
Pour Point, ° F.	−20	−25
Flash point, ° F.	340	340
Fire point, ° F.	385	385
Sulfur content, per cent	3.58	2.79

Other ingredients such as fatty oils, lead compounds, halogenated compounds, etc., may be incorporated as desired and those familiar with the prior art need no details as to their use.

This sulfur-bearing jojoba bean oil base may also be used in an absorbed oil as:

	Percent
Medium lime base grease	17.5
100-sec. mineral oil	75
Sulfurized jojoba bean oil	7.5
	100

Such an oil has a Furol vis./130° F. of about 90 seconds and a sulfur content of 2.84% while a similar absorbed oil using sulfurized sperm oil would carry only 2.24% sulfur.

When this sulfurized jojoba oil is incorporated into an S. A. E. 80 mild E. P. transmission and differential oil such as:

	Percent
600-second cylinder oil	91
Sulfurized jojoba base	7
Paraflow	2
	100

the sulfur content is 3.09% while a similar oil prepared from sulfurized sperm oil contains 2.54% sulfur.

In the case of a heavy E. P. gear oil such as the following:

	Percent
Latex treated mid-Continent bright stock	40
Mid-Continent bright stock	49
Lead naphthenate	3
Sulfurized jojoba base	8
	100

the sulfur content would be 3.13% while a similar product using a sulfurized sperm oil base would contain only 2.5% sulfur.

Another example of the use of this sulfur-bearing base is in an extreme pressure grease. An ordinary medium lime base grease is prepared in such a way as to contain 3% lead naphthenate and 15% sulfurized jojoba oil base. Here we would have a worked penetration of approximately 225 and a sulfur content of 4.81%. A corresponding grease prepared from sulfurized sperm oil would contain only 3.62% sulfur.

Saybolt Standard Universal Viscosities at 100° F. were run on most of the sulfurized oils shown in the examples as well as for their 50% and 10% solutions in 100-sec. mineral oil. The results are as follows:

Example	Base	50% soln.	10% soln.
2 (unblown)	4,748	678	152
2 (blown)	6,518	770	157
3 (unblown)	------	555	151
4 (unblown)	11,000	859	160
4 (blown)	21,380	1,201	165
5 (unblown)	10,887	832	159
5 (blown)	20,347	1,196	165
6 (unblown)	5,397	662	151
6 (blown)	7,878	758	155
7 (unblown)	8,364	802	158
7 (blown)	14,624	930	161
8 (unblown)	10,082	798	156
8 (blown)	18,743	1,188	164

In all examples where jojoba oil, hydrolyzed jojoba oil, or the components of jojoba oil were used, the color of the unblown oil in 10% solution in 100-sec. mineral oil on the ASTM colorimeter was 8. Blowing caused a slight darkening. Sulfurized sperm and lard oils gave 10% solutions which were far too dark to be measured even when unblown.

As described in the prior art, sulfurization in an inert atmosphere results in a lighter colored product. Thus when Example 3 is carried out in an atmosphere of CO_2, a 10% solution in 100-sec. mineral oil has an ASTM color of between 6 and 7. A 20% solution showed a color of 8, and a 5% solution of the original Example 3 had a color of between 6 and 7.

Sulfur analyses show the difference in the various oils very sharply. Analyses were made on 10% solutions in 100-sec. mineral oil using the Parr peroxide bomb. The sulfur content of the base (oil obtained in the various examples) was calculated and from this figure the sulfur content of the fatty matter alone was determined. The 100-sec. mineral oil used as solvent had a sulfur content of 0.87% and the 300-sec. mineral oil used in the base also had a sulfur content of 0.87%.

Example	In 10% soln.	Sulfur Content	
		In Base	In Fatty Oil
2	2.96	21.80	23.6
3	3.06	22.80	25.0
4	2.79	20.00	25.1
5	3.05	22.70	24.9
6	3.04	22.60	24.8
7	3.04	22.60	24.8
8	3.61	28.30	30.8

As shown by Example 8, jojoba bean oil can take up almost 31% of sulfur whereas sperm oil (as well as other animal oils such as lard oil) takes up a maximum of 23.6%.

The liquid sulfurized compositions described herein contain up to about 31% of combined sulfur. This value is about 25% higher than the highest amount of sulfur that can be combined with sperm oil, the oil most nearly related to jojoba oil when molecular structure is considered. This value is also much higher than can be obtained with other oils such as lard oil. Furthermore, it is to be noted that high-sulfur liquid products (containing up to about 31% combined sulfur) can be obtained from jojoba bean oil without the need of cutting with a mineral oil, although, as pointed out above, mineral oils may be added if desired.

I claim:

The process of making a liquid highly sulfurized jojoba bean oil containing up to about 31% combined sulfur, which comprises heating jojoba bean oil and adding sulfur portionwise thereto on the up-heat between 250° F. and 400° F., whereby the reaction product when cold is a solid when formed with large amounts of sulfur, and thereafter continuing the heating at between 350° F. and 400° F. for up to about 20 minutes until the reaction product when cold is liquid.

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