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PROCESS FOR THE ACTIVATION OF NORMALLY LIQUID FATTY MATERIALS CONTAINING UNSATURATED COMPOUNDS

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The invention relates to a process for the treatment of normally liquid fatty materials containing unsaturated compounds such as drying oils, semi-drying oils and unsaturated oil fractions, particularly those containing a high content of isolated double bonds, at elevated temperature with sulphur dioxide under pressure as a catalyst.

It is known that by different conversions of oils, especially at elevated temperature, sulphur dioxide is an active catalyst. For instance it is known that it is possible to hard non-drying oils by heating them at temperatures of preferably 100–140° C. under such a sulphur dioxide pressure that the sulphur dioxide remains liquid. In this manner a cis-trans transformation is obtained by which a hardening is caused. An example of such a transformation is the transformation of oleic acid into elaidic acid. Under other circumstances of temperature and pressure drying oils can be polymerised and converted into polymerised oils with the use of sulphur dioxide as a catalyst.

We now have found that in using sulphur dioxide as a catalyst by an adequate choice of the circumstances, such as temperature, sulphur dioxide pressure, and duration of the treatment, it is possible to realise still another reaction in drying oils. By heating of drying or semi-drying oils containing isolated double bonds under sulphur dioxide pressure such a transformation of these oils can be obtained that the isolated double bonds of the acid groups of the drying oils are converted into conjugated double bonds. By this transformation the drying qualities of the oils are modified and linseed oils and oils having corresponding properties are converted into oils showing more resemblance with Tung oil which in general by its high content of conjugated double bonds is more reactive than linseed oil.

The normally liquid fatty materials containing unsaturated compounds, which can be treated according to our invention comprise drying oils, relatively highly unsaturated semi-drying oils, such as soja oil, sunflower oil and fish oils, and relatively highly unsaturated oil fractions, such as fractions of soja oil and herring oil. These relatively highly unsaturated oil fractions may for instance be obtained by separating solid fractions from oils, for instance by refrigeration or extraction or by application of the hardening process according to the British specification 502,390 after separating out the hardened products, or by a combination of these separating methods.

The activated conversion products obtained dry faster than the starting material, their addition of hydrochloric acid is easier and they have a higher diene value (addition of maleic acid anhydride). In contrast to Tung oil the dried film of activated oil does not show the characteristic ice flowers. Moreover the activated products are more resistant to water and sodium carbonate.

By the activation according to our invention polymerisation and formation of substances being solid at room temperature by cis-trans transformation only occur in a low degree. The viscosity of the treated oil shows only a small difference with that of the starting oil and the largest part of the activated product is distilled off by distillation in a high vacuum. The activated oil is further considerably more sensitive for high temperature than the starting oil. From the activated oil a polymerised oil can be prepared in a short time without use of a catalyst.

According to our invention activated oils are prepared by treating the starting oil containing no or a small amount of conjugated bonds in the acid groups at a temperature between approximately 160–230° C., preferably between 180 and 200° C., in the presence of sulphur dioxide, preferably under pressure. By using a higher sulphur dioxide pressure a lower temperature may be used, whereas by using lower pressures higher temperatures may be used. The influence of the temperature and the pressure is illustrated by Table I which relates to the heating of linseed oil under sulphur dioxide pressure for 1 hour.

Table I

Average pressure in kg/cm²	Average temperature in °C	Specific gravity (d^{20}_4)	Refractive index (n^{20}_D)	Iodine value	Acid value
Starting linseed oil		0, 9282	1, 4811	188, 5	.....
100	175	0, 9376	1, 4886	156	2, 2
34	182	0, 9318	1, 4859	171	2, 2
104	200	0, 9478	1, 4923	127	8, 4
33	208	0, 9504	1, 4920	117	10, 8
37	217	0, 9422	1, 4902	145	8, 0

For obtaining good yields the oil has to be treated for from 5 to about 10 minutes or more at the temperature mentioned. We have found, however, that the present conversion has a normal thermal coefficient, so that by the use of higher temperature the conversion can be considerably accelerated, as Table II shows for linseed oil.

Table II

Temperature in °C.	Pressure in kg/cm²	Reaction time in minutes	Proportion of the number of cm³ of oil (measured at room temp.) and the number of cm³ of liquid SO_2	Refractive index (n^{20}_D)	Specific gravity (d^{20}_4)
212	100	30	70:20	1,4917	0,9448
225	110	15	70:18	1,4918	0,9442
225	130	10	30:32	1,4914	0,9415
225–230	100–200	15	90:10	1,4911	0,9444

Finally Table III shows that the products prepared at for instance 190°C and 225°C correspond closely.

Table III

Temperature in °C	Reaction time in minutes	Pressure in kg/cm²	Refractive index (n^{20}_D)	Specific gravity (d^{20}_4)	Diene value
Starting linseed oil	----------		1,4813	0,9292	----
190	30	80	1,4873	0,9343	16
	45	75	1,4881	0,9349	17
	60	72	1,4889	0,9365	20
	90	70	1,4903	0,9396	20
225	8	90	1,4880	0,9363	18,5
	13	90	1,4909	0,9403	20,5
	22	100	1,4926	0,9545	18

By the use of an adequate high temperature, therefore, it is possible to accelerate the conversion in such a manner that the process can be continuously carried out.

It is recommendable to remove the peroxides from the unsaturated fatty oils previously to the heating with sulphur dioxide.

This can be carried out in a known manner by treatment at elevated temperature, for instance at 290°C and passing a stream finally divided indifferent gas, e. g. nitrogen, through the oil.

By application of our invention and an adequate choice of the temperature and the sulphur dioxide pressure besides the transformation of the isolated double bonds into conjugated double bonds only relatively small polymerisation and a small separating out of solid matter by cis-trans transformation occur.

The invention is further elucidated but not at all limited by the following examples:

Example I

In order to remove the peroxides present linseed oil is heated at 290°C under passage of a stream finally divided nitrogen through the oil. After treatment for a quarter of an hour the oil is cooled down to about 196°C, thereupon brought under a sulphur dioxide pressure of about 150 kg/cm² and heated for an hour under these circumstances at the temperature mentioned. The activated oil dries quicker than linseed oil, the film formed does not show the ice flowers being characteristic for Tung oil. The diene value is increased from about 2 to 25,5.

Example II

A linseed oil being treated according to Example I for the removal of the peroxides is heated during one hour at 175°C under a sulphur dioxide pressure of 100 kg/cm². The product obtained dries much faster than linseed oil, but does not form ice flowers.

Under lower sulphur dioxide pressure, however, already perceptible results can be obtained; for instance by heating at 193°C under a sulphur dioxide pressure of 42 kg/cm² a considerable increase of the diene value and of the drying velocity are obtained. Besides the acceleration of the drying and the transformation of the isolated double bonds into conjugated double bonds here also only a weak polymerisation and separation of only a small amount of solid matter by cis-trans transformation occur.

Example III

From soja oil a liquid fraction having a relatively high iodine value is prepared in the following manner. The soja oil is first heated during half an hour at 180°C under passage of a stream of nitrogen for the removal of the peroxides. Thereupon 550 g sulphur dioxide are added to 800 cm³ of the so-treated oil and the mixture is heated for 3 hours at 110–115°C. The reaction product is separated into a solid and a liquid fraction by crystallisation from acetone. The liquid fraction then is activated according to our invention by heating at about 200°C under a sulphur dioxide pressure of 75–80 at for one hour. Table IV gives a comparative survey of the properties of the several products involved.

Table IV

Product	Percent	Technical melting point in °C	Acid value	Iodine value	Refractive index (n^{20}_D)	Spec. gravity (d^{20}_4)	Drying test (entirely dry after:)	Viscosity in poises (20° C)
							Days	
Soja oil	------	----------	0,3	136,5	1,4759	----------	----------	----------
Reaction product hardened with SO_2	------	18,9	0,5	135	1,4751	----------	----------	----------
Obtained by crystallisation from acetone:								
Solid fraction	37	26,1	----------	111	1,4720	----------	----------	----------
Liquid fraction	63	----------	0,6	148,5	1,4763	0,9217	9	1
Liquid fraction activated with SO_2	------	----------	----------	124	1,4840	0,9302	3,5	2

Various changes may be made in the details disclosed in the foregoing specification without departing from the invention or sacrificing the advantages thereof.

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