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⑤④ **Process for the solvent fractionation of olive oil stearine and related products.**

⑤⑦ The process resides in dissolving stearine in a hydrocarbon solvent and in heating the mixture while stirring until all the stearine is in solution. After slowly cooling down to the crystallization temperature, the stirring is stopped and the precipitate is collected and filtered and the collected precipitate and filtrate are individually processed in conventional evaporators and deodorizers, while the solvent is recovered at the same time. The yield is a high melting solid fat and semisolid material having a lower melting point suitable for a confectionary fat.

When the solvent used is acetone, the collected precipitate is washed with fresh acetone and added to the filtered which is then subjected to a further crystallization. With such a two-step process a fraction is obtained formed by a high melting solid fat, by a semisolid material having a lower melting point and a by a clear and bright oil. Also in this case the semisolid fat material is suitable for a confectionary fat.

PROCESS FOR THE SOLVENT FRACTIONATION OF OLIVE OIL
STEARINE AND RELATED PRODUCTS

This patent for industrial invention relates to a process for the solvent fractionation of olive oil stearine and to the related products.

5 Olive oil stearine, a high melting fatty material, is a by-product of the edible oil industry.

The physical properties of this material are such that it has few uses as a food material although it is available on large quantities at prices well below other fats and oils.

10 The object of the invention is the taking of this economically unattractive fatty material and by virtue of expertise of Applicant in oil and fat technology create new, useful and more valuable fatty products.

15 While these products will be extremely useful themselves, their utility is not restricted to only their individual use. In fact their greatest economical and technological value may be in their use with other fats, or in combination with other fats or non-fatty materials.

20 In this invention the processes to fractionate olive oil stearine will be disclosed. These processes use simple solvent crystallization techniques to resolve the stearine into glyceride fractions of contrasting physical properties. One of the objectives has been to produce a practical, inexpensive confectionary fat. The confectionary fat industry
25 has for many years sought an inexpensive, replacement fat for the expensive cocoa butter. Cocoa butter is the ideal confectionary fat since it is a solid at room temperature but melts sharply and completely at body temperature. It owes its unique physical properties to its component glycerides. These glycerides are largely unsaturated
30 unsaturated glycerides of palmitic, stearic and oleic acids together with lesser amounts of diunsaturated monosaturated glycerides, and triunsaturated glycerides of the same fatty
35 acids. Thus, cocoa butter is a very complex mixture of glycerides and it is not unreasonable that olive stearine which contains the same fatty acids and many of the same glycerides might be fractionated to yield a fraction whose glycerides have melting properties similar to cocoa butter.

40 Olive oil stearine according to its DSC (Differential Scanning Calorimetry) melting profile of Figure 1 has a melting range from 55°-70° C so it obviously contains some very high melting glycerides. Consequently, according to the present invention, the solvent fractionation process is carried out

to remove a substantial amount of these high melting glycerides leaving behind a fraction of mixed glycerides of more appropriate lower melting properties. The processes of this invention may be carried out by either the 'batch' or 'continous' fraction process or combination of these but only the 'batch' process will be cited in the examples.

In any solvent fractionation process the choice of solvent is most important and although several solvents may be used, hydrocarbon solvents with boiling range under 130° C or acetone are preferred solvents of the examples. Solvents such as methyl alcohol, ethyl alcohol, isopropyl alcohol acetone, methyl ethyl ketone, methyl isobutyl ketone, 1-nitropropane, 2-nitropropane, and various mixtures of these solvents may be used providing appropriate changes are made in the fat to solvent ratio and temperature of crystallization.

Although the chemical nature of the olive oil stearine is important, the physical nature of the fractions dictates the eventual utility of the fractions and is thus of foremost importance.

Consequently, it will be described the physical nature of the fractions primarily by the technique of Differential Scanning Calorimetry (DSC) in which melting behavior of the product is graphically depicted as a melting profile as the product changes with heating from a solid to a liquid state. To define the chemical nature of the fractionation products, it is preferred to analyze the products by gas liquid chromatography to determine the fatty acid compositions. The combination of these two techniques will adequately serve to characterize the fractionation products.

The fatty acid composition of a typical olive oil stearine is given in the following table:

	<u>Fatty Acid</u>	<u>Percent by Weight</u>
	C-16	21.7
35	C-16:1	0.6
	C-18	4.5
	C-18:1	62.5
	C-18:2	10.4

while the thermal properties of the stearine are graphically depicted by the Differential Scanning Calorimetry (DSC) profile in Figure 1.

The stearine is not a brittle solid but is high melting which indicates a preponderance of high melting glycerides mixed with many lower melting glycerides. It is obvious that fatty materials of this type lend themselves to solvent

crystallization processes for the production of fractions with specific physical properties.

5 In the present process, the olive oil stearine is melted and dissolved in hot solvent at a ratio 2 to 10 liters per kilo of stearine. If hydrocarbon solvent is used, it may be of any boiling range up to 130° C but the mixture with boiling range of about 70° C is preferred especially for ease of solvent recovery. The solvent fat mixture is warmed to about 60° C to insure complete solution. It is then allowed to
10 cool to the crystallization temperature with or without stirring. Cooling of the mixture can be effected in any of several ways. The crystallizer may be equipped with appropriate cooling coils or the crystallizer might be held in a thermo-stated room.

15 Stirring of the mixture will speed up the heat transfer process and permit crystallization equilibrium to be reached readily. If stirring is not used, the crystallization process for large batches may take from 6 to 12 hours to reach equilibrium. However, with appropriate stirring, crystallization
20 equilibrium may be reached in less than two hours.

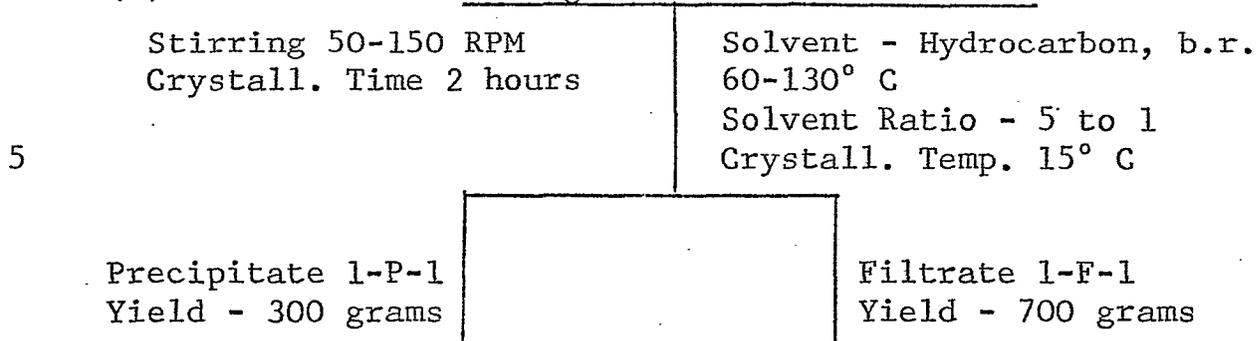
The precipitate may be collected by either vacuum or pressure filtering or by centrifugation or by decantation or by a combination of these techniques.

25 The collected precipitates should be washed with fresh solvent at least 2° C cooler than the crystallization temperature. Efficient washing of the precipitate will produce sharply dedefined fractions as well help to maxime the yield.

30 The fractions may also be carried out in a much shorter time interval in a continous system by utilizing high speed, scrape surface crystallizers. The number of the crystallization steps will depend on the nature and number of desired fractions.

35 Several processes have been devised for the fractionation of olive oil stearine. One, using a hydrocarbon solvent is a very simple one-step process which produces two principal products, a high melting solid fat in a 30% yield, and a 70% yield of a softer, semisolid fatty material suitable for a confectionary fat. The process is detailed in Example 1 out-lined hereinafter:

(A) 1000 grams Olive Oil Stearine



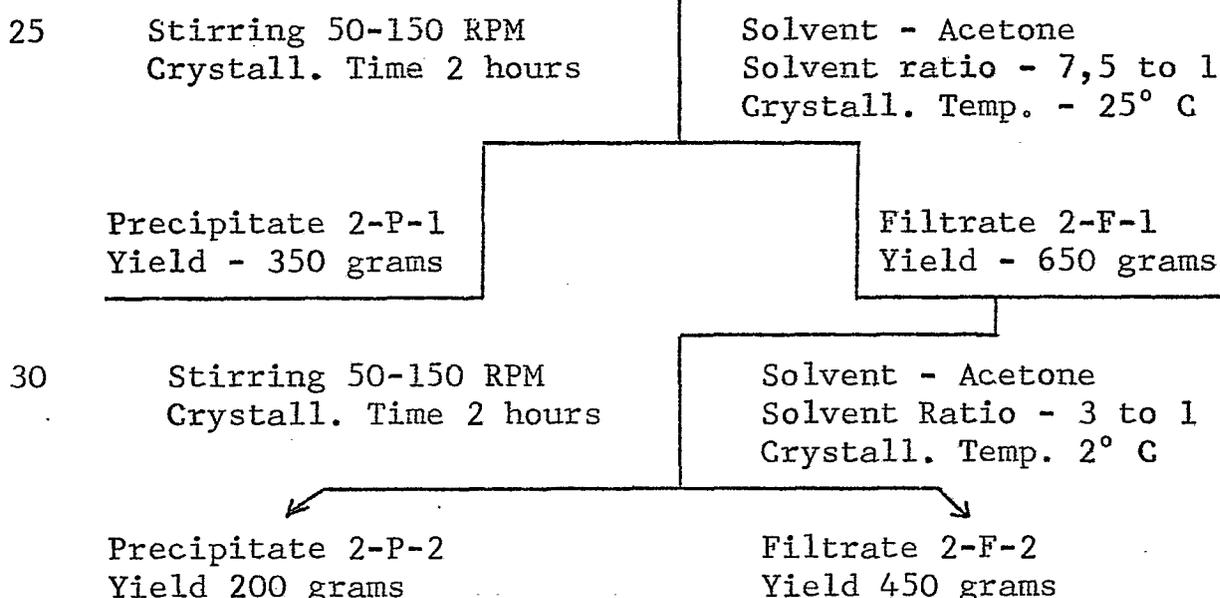
The fatty acid composition of these products are listed hereinafter:

Fatty Acid	Percent by Weight	
	Fr. 1-P-1 High Melt Solid Fr.	Fr. 1-F-1 Semisolid Fr.
C-16	67.3	15.1
C-16:1	-	1.0
C-18	11.4	3.4
C-18:1	17.3	67.7
C-18:2	-	12.8
C-20	3.0	0.3

Figure 2 shows the DSC melting profile of the high melting solid fat (1-P-1) while Figure 3 gives the DSC melting profile for the softer, semisolid fat (1-F-1).

Another fractionation process is detailed in Example 2 and outlined hereinafter:

(B) 1000 grams - Olive Oil Stearine



In this two-step process, olive oil stearine with acetone as the solvent is resolved into three fractions. One is a high

melting solid fat (2-P-1), a lower melting semisolid fraction (2-P-2), and a clear, bright oil similar in many respects to the original olive oil (2-F-2). The fatty acid compositions of these fractions are listed hereinafter:

5 (C) Percent by Weight

<u>Fatty Acid</u>	<u>Fr. 2-P-1 High Melt Solid Fr.</u>	<u>Fr. 2-P-2 Semisolid Fr.</u>	<u>Fr. 2-F-2 Oil Fr.</u>
C-16	69.0	60.2	12.7
C-16:1	-	1.0	1.1
10 C-18	10.5	8.8	2.9
C-18:1	14.1	19.8	71.0
C-18:2	-	8.1	11.3
C-20	3.5	0.4	0.2

15 The thermal characteristic of the fractions as defined by DSC are shown in Figures 4,5 and 6, respectively.

20 The soft, semisolid glyceride fractions thus isolated were found to be compatible with cocoa butter since when mixed with cocoa butter they did not distort the original melting characteristics of cocoa butter. The DSC melting profile for pure cocoa butter is shown in Figure 7, and for comparison the DSC melting profiles of the mixture of 85% cocoa butter and 15% olive oil stearine confectionary fat (1-F-1) and (2-P-2) are presented in Figures 8 and 9. The DSC melting profiles of the mixtures show little distortion of the characteristics shown by the pure cocoa butter. It has been also mixed the olive oil confectionary fat in standard dark chocolate formulations at the 15% level of total fat and found the resultant products to have excellent properties, equal to chocolate containing only pure cocoa butter.

30 While the crystallization process may consist of multisteps, it is preferred to illustrate the concept of the invention by only two single crystallization schemes. Example 1 will illustrate a process with the maximum yield of a confectionary fat fraction while Example 2 will illustrate a process with maximum yield of the oil fraction.

35 EXAMPLE 1 (One-step process)

The process and the fractions yields are indicated in the scheme (A) above. One kilo of olive oil stearine is dissolved in 5 liters of hydrocarbon solvent (b.p. under 130° C). The mixture is warmed while stirring to about 60° C until all of the stearine is in solution. The solution is allowed to cool slowly with stirring at a rate of 50-150 RPM. The coolant circulated through the coils of the crystallizer should not be at more than 10° C lower temperature than the crystallization mixture. When the desired temperature is reached

ched (15° C), the stirring is stopped and the mix is held at this temperature for a short time to insure crystallization equilibrium. For small factory batches, this may be only 15 minutes in a two hours crystallization period while for larger plant size batches, one hour in a 8-12 hours crystallization period would be sufficient. The precipitate is collected by filtering under vacuum or pressure. The collected precipitate and filtrate are individually processed in conventional evaporators and deodorizers and the hydrocarbon solvent is recovered at the same time. The yield of the high melt solid fraction is 300 grams or 30% and the melting characteristics of this material are shown by the DSC melting profiles in Figure 2. The yield of the softer, lower melting confectionary fat fraction is 700 grams or 70%. The melting characteristics of the confectionary fat fraction (1-F-1) are illustrated by the DSC melting profile of Figure 3.

EXAMPLE 2 (Two-step process)

The two-step process for the fractionation of olive oil stearine using acetone as the solvent is outlined in the scheme (B) above which also indicates solvent ratios and fraction yields. One kilo of olive oil stearine is dissolved in 7.5 liters of hot acetone. The mixture is stirred and warmed to about 52° C until all of the stearine is in solution. The solution is allowed to cool with stirring (50-150 RPM) while the crystallizer is held at 25° C. When this temperature is reached, the stirring is discontinued and the mixture of solvent and crystal is held for a short time to insure crystallization equilibrium. The precipitate (2-P-1) is collected and washed with fresh acetone previously cooled to about 23°C and equal to about 10% of the original crystallization volume. This solvent wash is added to the filtrate (2-F-1) prior to the next crystallization step. The combined filtrates are returned to the crystallizer, the solvent ratio is adjusted to a ratio of 3 liters of acetone per kilo of filtrate. The solution is allowed to cool with stirring until the final crystallization temperature of 2° C is reached. The crystalline precipitate is collected and washed at one or more times with a volume of fresh acetone at 0° C equal to about 10% of the original crystallization volume. The collected precipitate and filtrate are processed individually by conventional evaporators and deodorizers. The yield of the high melt fraction (2-P-1) is 350 grams or 35%, the yield of the softer, semisolid fraction (2-P-2) is 200 grams or 20% and the yield of the remaining

material, the oil fraction (2-F-2) is 450 grams or 45%. The thermal characteristic of the fractions as defined by Differential Scanning Calorimetry are shown in Figure 4, for the high melt fraction (2-P-1), Figure 5 for the softer semisolid fraction (2-P-2), and Figure 6 for the oil fraction (2-F-2). The fatty acid compositions of the fraction are given in Table (C) above.

Claims:

- 1) A process for the solvent fractionation of olive oil stearine according to the scheme (A) and described in Example 1 in which the solvent is a mixture of hydrocarbons with boiling point under 130° C.
- 2) A process according to claim 1 in which the solvent is ethyl methyl ketone or methyl isobutyl ketone.
- 3) A process according to claim 1 in which the solvent is 1 or 2 nitropropane.
- 4) A process according to claim 1 in which the solvent is methyl, ethyl or isopropyl alcohol.
- 5) A process for the solvent fractionation of olive oil stearine according to the scheme (B) and described in Example 2 in which the solvent is acetone.
- 6) A process according to claim 5 in which the solvent is methyl ethyl ketone or methyl isobutyl ketone.
- 7) A process according to claim 5 in which the solvent is 1 or 2 nitropropane.
- 8) A process according to claim 5 in which the solvent is methyl, ethyl or isopropyl alcohol.
- 9) A high melting glyceride fraction, m.p. 60°-70° C, obtained by the processes in claims 1 through 8.
- 10) A semisolid glyceride fraction of melting point under 46° C obtained by the processes in claims 1 through 8.
- 11) An oil fraction with solidification point under 10° C obtained by the processes in claims 5 through 8.
- 12) A confectionary fat comprising of 1-99% of the fat fraction in claim 10 and 99-1% of cocoa butter or any other confectionary fat.
- 13) A cosmetic or pharmaceutical fatty base material comprising the high melting glyceride material in claim 9.
- 14) A cosmetic or pharmaceutical fatty base material comprising the semisolid glyceride fraction in claim 10.
- 15) A source of palmitic or stearic acid obtained by the chemical or enzymatic hydrolysis of the high melting glyceride fractions obtained by the processes in claims 1 through 8.
- 16) A source of oleic acid obtained by the chemical or enzymatic hydrolysis of the low melting glyceride fraction obtained by the processes in claims 10 and 11.
- 17) A source of the unsaturated hydrocarbon squalene isolated from the low melting glyceride fraction obtained by the processes in claims 10 and 11.

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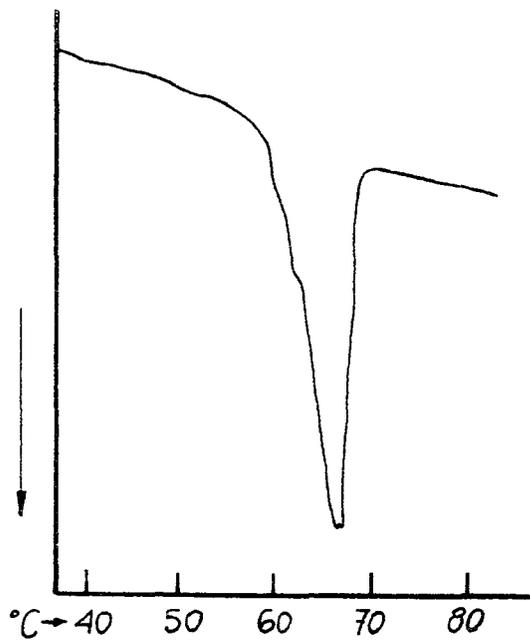


Fig. 1

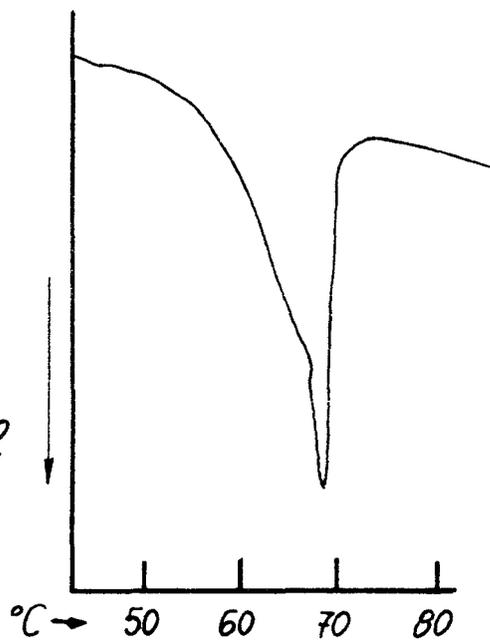


Fig. 2

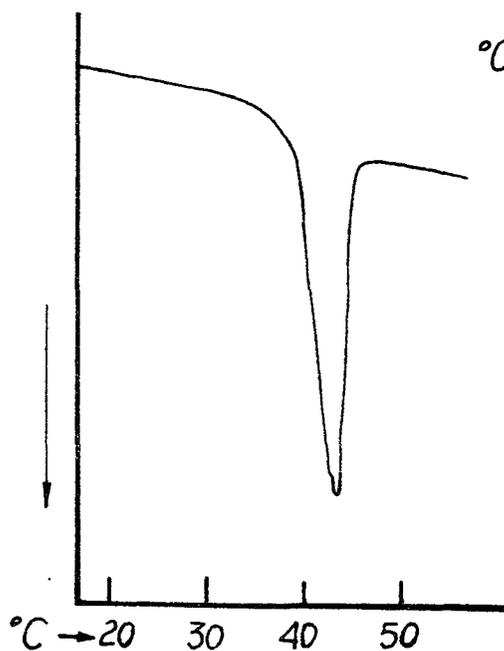


Fig. 3

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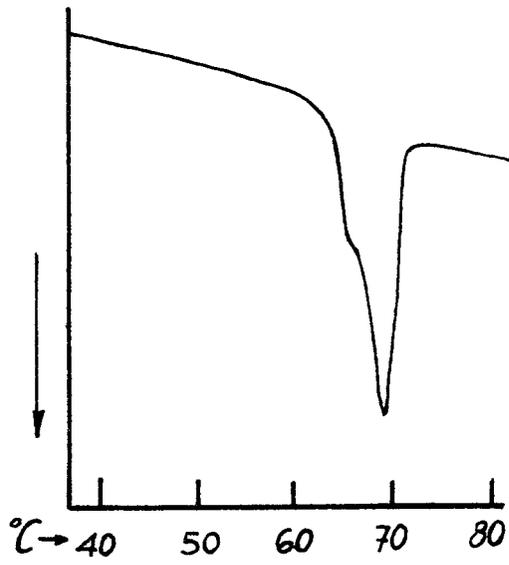


Fig. 4

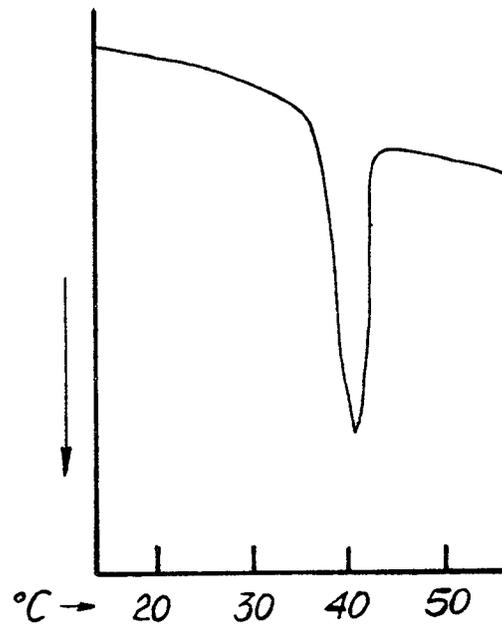


Fig. 5

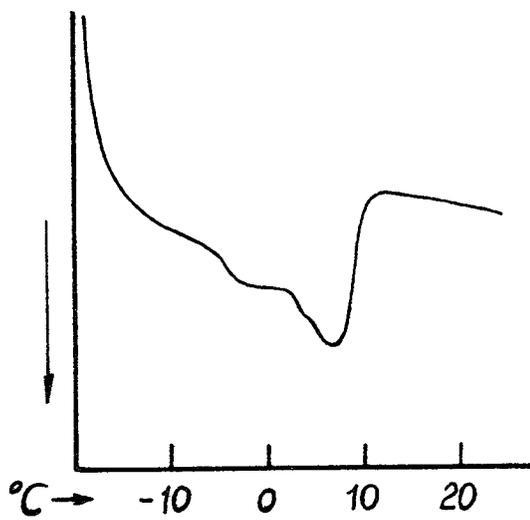


Fig. 6

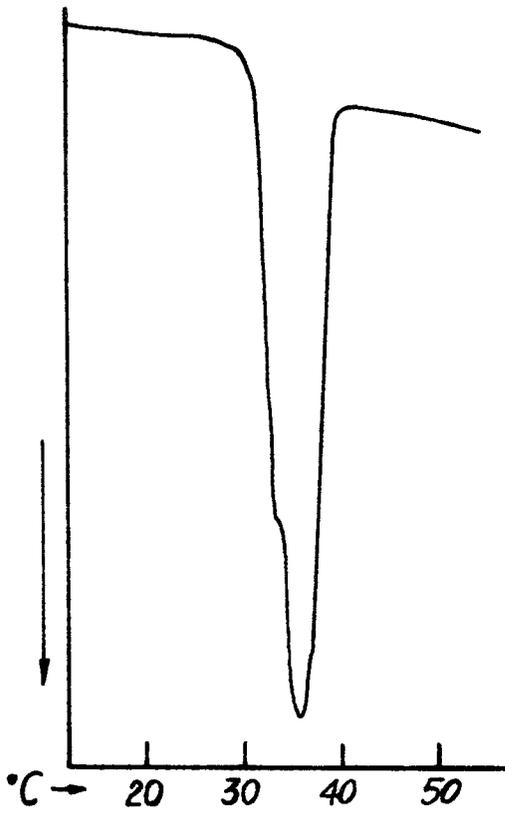


Fig. 7

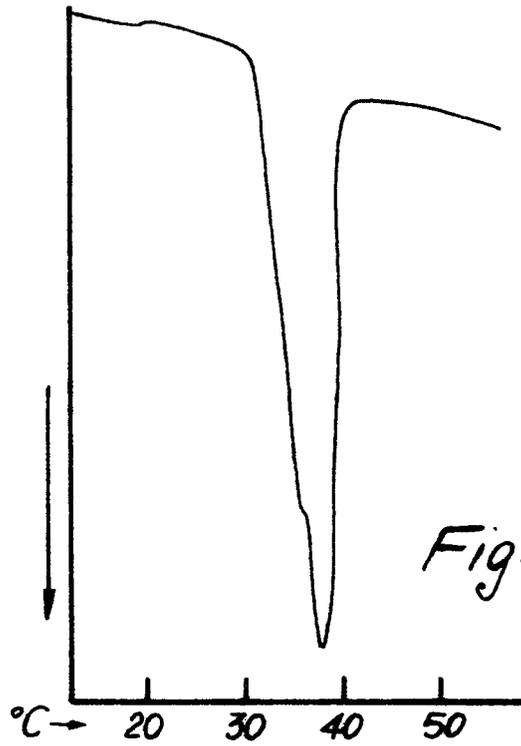


Fig. 8

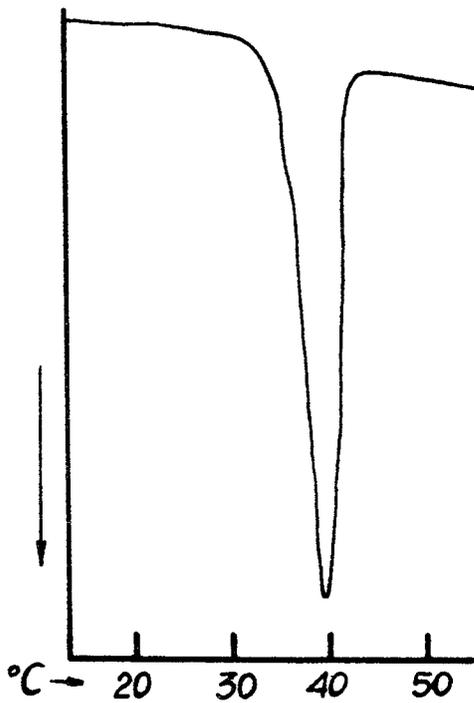


Fig. 9



DOCUMENTS CONSIDERED TO BE RELEVANT		CLASSIFICATION OF THE APPLICATION (Int. Cl.)	
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
	<p><u>FR - A - 2 427 386</u> (LESIEUR-COTELLE & ASSOCIES)</p> <p>* Page 11, line 35 - page 12, line 32; examples 1-4 *</p> <p style="text-align: center;">--</p> <p><u>GB - A - 750 045</u> (TEXACO DEVELOPMENT CORP.)</p> <p>* Page 1, lines 34-87; page 2, lines 81-100; claim 1 *</p> <p style="text-align: center;">--</p> <p><u>US - A - 3 431 116</u> (R.O. FEUGE et al.)</p> <p>* Column 4, line 20 - column 7, line 57; claim 1 *</p> <p style="text-align: center;">----</p>	<p>1,4, 9-12</p> <p>1-3, 9,10</p> <p>1,9, 10,12</p>	<p>C 11 B 7/00</p> <p>TECHNICAL FIELDS SEARCHED (Int. Cl.)</p> <p>C 11 B 7/00 A 23 D 5/00 A 23 G 1/00</p> <p>CATEGORY OF CITED DOCUMENTS</p> <p>X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons</p> <p>&: member of the same patent family, corresponding document!</p>
<p> The present search report has been drawn up for all claims</p>			
Place of search	Date of completion of the search	Examiner	
The Hague	05-06-1981	SCHUERMANS	