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(54) LIQUID CRYSTAL COMPOSITIONS

(71) We, BECTON, DICKINSON AND COMPANY, a corporation organised and existing under the laws of New Jersey, United States of America, of: Rutherford, New Jersey, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The invention relates to temperature indicating compositions and more particularly relates to liquid crystal compositions, their use and temperature sensing devices employing them as indicator compositions.

Temperature sensing devices including temperature recorders employing cholesteric liquid crystal compositions as the temperature sensitive indicator are generally well known; see for example U.S. Patents 3,704,625 and 3,974,317. Such devices function by virtue of a color change exhibited by the liquid crystal indicators under certain temperature conditions. Liquid crystals are compounds which possess a so-called mesomorphic phase (sometimes referred to as the "mesophase"), intermediate between their solid crystal form and their isotropic liquid form. The mesomorphic phase of cholesteric liquid crystals is highly colored due to the periodic structure of the phase.

The color exhibiting cholesteric liquid crystals are optically active and are said to be "optically negative". The observed colour of the cholesteric liquid crystal in its mesomorphic phase is a function of its chirality or "twist" which will be described in more detail hereinafter. Other liquid crystal compounds such as nematic type liquid crystals are said to be optically positive in the mesomorphic state and do not exhibit a specific color associated with periodic structure. It was heretofore known that one could admix-cholesteric type liquid crystals with nematic type liquid crystals to impart chirality and therefore visibility to the mesomorphic phase of the resultant liquid crystal composition; see for example U.S. Patents 3,650,603 and 3,984,343.

In general, the prior art temperature sensing and recording devices employing liquid crystals as the temperature indicator have not been entirely satisfactory for a number of reasons. For example, many liquid crystal indicator compositions are unstable and have short shelf lives. This is particularly true of mixtures of liquid crystals with so-called liquid transition point "elevator" or "depressant" additives which are heterogeneous mixtures and which tend to separate on standing. Many of such compositions which include hydrocarbon additives are particularly unstable. The hydrocarbon additives destroy crystallinity of the liquid crystals over prolonged periods of contact. After a relatively short period of time, the liquid transisition points of such compositions will have shifted. Therefore, unless the temperature sensing device employing such a composition is used fairly rapidly after its manufacture, inaccurate results will be obtained. Another difficulty heretofore encountered with the prior art compositions is that the temperature range over which a given liquid transition point occurs may be so broad as to render the device useless for certain purposes, for example as a replacement for a medical clinical thermometer where accuracy within plus or minus 0.5°F. is desired. Many prior art temperature sensing devices using liquid crystal temperature indicators are too insensitive to measure such small differences in temperature.

The liquid crystal based temperature sensing compositions of this invention are relatively stable over long periods of time even if the ingredients are relatively impure. They also pass through their liquid transition points very rapidly and over relatively narrow temperature ranges. In other words, the liquid transition points for the liquid crystal compositions of my invention are very sharp and occur at or very near to any specific desired temperature point. In addition, the compositions of this invention exhibit controlled hysteresis and are therefore particularly suited for use as a disposable temperature recorder for clinical medical use. The compositions of the invention also provide a means of color control is visually indicating temperature sensing devices.

Mixtures of cholesteric type liquid crystals with nematic type liquid crystals have heretofore been known in the prior art; see for example U.S. Patents 3,650,603; 3,666,881; 3,720,623; 3,923,685; 3,931,041; 3,956,169; 3,973,830; and RE 28,806. Other U.S. patents representative of the prior art are 3,114,830; 3,529,156; 3,716,289; and 3,997,463.

Broadly speaking the temperature indicating compositions of this invention comprise in admixture:

a) an optically active cholesteric liquid crystal compound which is chemically inert with respect to other components of the composition; and

b) a mixture of at least two different nematic liquid crystals having liquid transition points within 20°C of each other and each being an ester selected from the following:
4-alkylphenyl-4-alkoxybenzoates,
4-alkylphenyl-4-alkylbenzoates,
4-alkoxyphenyl-4-alkylbenzoates, and
4-alkoxyphenyl-4-alkoxybenzoates;

the proportion of a) being such that the composition selectively scatters light from the visible spectrum and exhibits a colour at temperatures below the liquid transition point but which ceases to scatter light from the visible spectrum and becomes colourless at temperatures above the liquid transition point.

The invention also comprises a temperature sensing device comprising an opaque support on which is or are disposed one or more such temperature indicating compositions.

The term 'liquid transition point' as used throughout the specification and claims means the point of temperature at which a liquid crystal compound or liquid crystal composition passes from the mesomorphic phase to the form of an isotropic liquid. This temperature point is also referred to occasionally by those skilled in the art as a 'clearing point'. The 'inert' is used herein to mean that the optically active compound will not chemically react with the nematic type of liquid crystal it is to be mixed with, nor will it adversely affect the desired properties of the compositions of the invention under conditions of use, as will be described more fully hereinafter. Advantageously the optically active cholesteric compound will be soluble in the compositions of the invention. The optically active cholesteric compounds employed as ingredients of the compositions of the invention are those having sufficient "twist" or chirality to provide visibility to the compositions of the invention in the mesomorphic phase. The term "twist" as used herein refers to the phenomenon observed when an optically active species is introduced into a nematic liquid. The nematic liquid takes a twisted configuration in all cases at low concentration and most cases at high concentration. The pitch of the twist is inversely proportional to the molar concentration of the optically active additive (the pitch is related to the wavelength of light scattered by the index of refraction of the liquid crystal; Pitch=n λ_{max}). Thus

$$P = \frac{T}{\text{mole fraction of optically active compound}}$$

wherein T is the constant of proportionality and is a material parameter. The optically active compounds employed as ingredients in the compositions of the invention will have a twist such that,

$$\frac{T}{n} < 550\ \mu$$

where n is the index of refraction of the liquid crystal ingredients.

In the accompanying drawings, to which reference is made later,

Figure 1 is a graph depicting the linearity of liquid transisition points in a series of compositions of the invention.

Figure 2 is a graph depicting the linearity of the liquid transition points in another series of compositions of the invention.

Figure 3 is an isometric view of a device of the invention employing compositions of the invention as temperature indicators.

Figure 4 is a cross-sectional side elevation along line 4-4 of Figure 3.

The cholesteric liquid crystals used in this invention are well known compounds as is the method of their preparation. A comprehensive description of such cholesteric type liquid crystals and their structure may be found in 'molecular structure and the properties of liquid crystals', Gray, Academic Press, 1962. Preferably the cholesteric compounds are compounds having a high or short wavelength pitch.

As indicated the degree of twist imparted by the optically active cholesteric compound to the compositions of the invention is important. Illustrative of cholesteric liquid crystals having suitable twist are cholesteryl oleyl carbonate, cholesteryl oleate, sitosteryl oleyl carbonate, cholesteryl phenyl. carbonate, cholesteryl sebecate, cholesteryl phenylacetate and stigmasteryl oleyl carbonate.

Advantageously the cholesteric compounds used in the compositions in this invention have liquid transition points near the event temperature to be indicated, i.e. within 25-35°C., preferably 20-25°C of the desired event temperature indication.

In the compositions of this invention, mixtures of at least two different nematic type liquid crystals are employed as the nematic type liquid crystal ingredient. Specifically the nematic liquid crystals are esters selected from

4-alkylphenyl-4-alkoxybenzoates,
4-alkylphenyl-4-alkylbenzoates,
4-alkoxyphenyl-4-alkylbenzoates and
4-alkoxyphenyl-4-alkoxybenzoates.

Preferred compositions are those containing at least two 4-alkylphenyl-4-alkoxybenzoates.

The blend of two different nematic liquid crystals provides a liquid crystal composition with a liquid transition point intermediate that of the individual liquid crystals. The proportions of the two nematic liquid crystals may be varied so as to obtain a number of compositions with a range of intermediate liquid transition points. In this manner, it is possible to obtain a plurality of liquid crystalline compositions differing in liquid transition points but only differing in composition by the proportion of nematic ingredients. This provides a plurality of indicating compositions which are uniform in structure and behaviour. In addition, since the liquid transisition point for each composition prepared is in direct proportion to the molar ratio of nematic type liquid crystal ingredients, one can prepare a series of compositions with a linear range of liquid transisition points. In fact, having determined the end points of the desired range of liquid transisition points, one can prepare the compositions of the invention which will provide the intermediate liquid transisition points by a simple calculation of the molar ratios of the ingredient nematic type liquid crystals. This is a valuable manufacturing advantage.

The compositions of the invention may be prepared by simple admixture of the above described ingredients. For example, the procedure for obtaining a stable, homogeneous mixture of nematic and cholesteric type liquid crystals is well-known to those skilled in the art; see for example the procedure described in the U.S. Patent 3,650,603. In general, the procedure comprises placing the desired proportions of fairly pure ingredient compounds in an appropriate vessel and heating them while stirring until a uniform isotropic liquid solution is obtained. The isotropic liquid is then allowed to cool slowly to room temperature. During cooling, the mixture enters a mesomorphic state. Stirring while the ingredients are in the isotropic liquid solution form is advantageous for obtaining homogenity of mixture. The homogenity of the mixture is advantageous.

The proportion of optically active cholesteric compound to nematic type of liquid crystals employed in the preparation of the compositions of the invention is important. In general, sufficient optically active compound is provided to impart color to the compositions of the invention in their mesomorphic phase. The optimal proportion will depend on the degree of twist found in the opticaly active compound. The optimal proportion may be found by trial and error technique as those skilled in the art will appreciate. More specifically, the proportion of optically active compound should be such as to provide a concentration thereof whereby pitch, as determined by twist, divided by the index of refraction multiplied by the mole fraction of optically active ingredient is from 440 to 680 μ, preferably from 480 to 600 μ. Usually, the proportion of cholesteric liquid crystal compound will lie within the range of from 25 to 60 percent by weight of the total composition.

Although the use of a single optically active compound gives the desired results in the compositions of the invention, mixtures of such compounds, for example mixtures of the above described cholesteric liquid crystals may be used as the optically active, inert ingredient.

Representative of preferred combinations of nematic liquid crystals which may be employed in the compositions of the invention are those listed below in *Table 1* together with their individual liquid transition points.

TABLE 1

Nematic Crystal Mixtures	Liquid Transition Point (C°)
4-n-pentylphenyl-4-n-pentyloxybenzoate	55°
and	
4-n-pentylphenyl-4-n-methoxybenzoate	42°
or	
4-n-pentylphenyl-4-n-methoxybenzoate	42°
and	
4-n-butylphenyl-4-n-heptylbenzoate	15°
or	
4-n-hexyloxyphenyl-4-n-butylbenzoate	50°
and	
4-n-heptyloxyphenyl-4-n-butylbenzoate	43°

As stated previously, by the blending of different molar proportions of the different nematic type liquid crystals, one can obtain a plurality of nematic liquid crystal compositions having a range of liquid transition points intermediate to the liquid transition points of the ingredient nematic type liquid crystals. The range is linear and in direct relationship to the molar proportions of component liquid crystals. Addition of the required proportion of optically active, inert compound will generally depress somewhat the liquid transition point observed for the mixtures of nematic type liquid crystals but this does not destroy the linear relationship described above. However, in order not to erode the sharpness of the liquid transisition points in the compositions of the invention the liquid transisition point of the cholesteric liquid crystal is preferably selected so as to be within about 20 degrees centigrade of that of the mixture of nematic type liquid crystals. Thus, one can select proportions of the ingredients of the compositions of the invention so as to obtain predictable liquid transisition points along a linear scale. This is a manufacturing advantage enabling one to select desired temperature end points and then predict compositional mixtures which will give intermediate liquid transisition points between the end points.

The following examples illustrate the invention but are not be construed as limiting. All parts and percentages are by weight.

Example 1

A series of compositions A-G are prepared by mixing 60 parts of varying molar proportions of 4-n-pentylphenyl-4-n-pentyloxybenzoate (PPPOB) and 4-n-pentylphenyl-4-n-methoxybenzoate (PPMeOB) with 40 parts of cholesteryl oleyl carbonate. The cholesteryl oleyl carbonate has a pitch of 325 mμ. The mixtures are heated to a temperature of circa 100°C. while stirring to obtain a homogeneous mixture. The mixtures are then allowed to cool to room temperature. The proportions of PPPOB/PPMeOB for each mixture, their liquid transisition points and the colors of the mixtures below their liquid transisition points are shown in *Table II*. below.

TABLE II

Mixture	Composition	Liquid Transition Temp. (C°)	Color	Mole Fraction PPMeOB
B	40% OCC 50% PPMeOB 10% PPPOB	36.8°	Red	.85
C	40% OCC 40% PPMeOB 20% PPPOB	38.5°	Red	.70
D	40% OCC 30% PPMeOB 30% PPPOB	40.2°	Red	.54
E	40% OCC 20% PPMeOB 40% PPPOB	41.9°	Red ↓ Green	.37
F	40% OCC 10% PPMeOB 50% PPPOB	43.5°	Red ↓ Green	.19

Upon heating the mixtures B-F to their liquid transition points, the color disappears as an indication that the indicated temperature has been reached. The compositions exhibit hysteresis.

Referring now to Figure 1, one may observe the graph plotting (light, upper line) showing the linearity of the liquid transition points for the compositions (B) through (F) prepared as described above. The compositions (B) through (F) as shown above are useful as the indicating compositions for a liquid crystal clinical temperature recorder employable for medical diagnosis.

Example 2

Repeating the procedure of *Example 1 supra.*, but changing the proportion of cholesteryl oleyl carbonate to 50 parts and reducing the proportion of PPPOB and PPMeOB to 50 parts, a series of compositions of the invention H-L is prepared. The composition, liquid transition point and color for each mixture is shown in *Table III* below.

TABLE III

Mixture	Composition	Liquid Transition Temp. (C°)	Color	Mole Fraction PPMeOB
H	50% OCC 40% PPMeOB 10% PPPOB	35.9°	Green	.83
I	50% OCC 30% PPMeOB 20% PPPOB	37.9°	Green ↓ Blue	.64
J	50% OCC 25% PPMeOB 25% PPPOB	39.0	Green ↓ Blue	.54
K	50% OCC 20% PPMeOB 30% PPPOB	39.6°	Green ↓ Blue	.44
L	50% OCC 10% PPMeOB 40% PPPOB	41.9°	Blue	.22

The compositions H-L, upon heating to the liquid transition point lose color. The compositions H-L exhibit hysteresis.

Referring again to Figure 1, one may observe the linear graph plotting showing the liquid transition points for the compositions (H) through (L) (heavy, lower line) prepared as described above. The compositions (H) through (L) as shown above as useful as the indicating compositions for a liquid crystal clinical temperature recorder, useful in medical diagnosis.

Example 3

Repeating the procedure of *Example 1, supra.*, but replacing the cholesteryl oleyl carbonate as used therein with an equal proportion of cholesteryl oleate (Pitch ≈325mμ), a series of compositions of the invention identified as N-Q is prepared. The compositions, liquid transition point and color for each mixture below its liquid transition point is shown in *Table IV*, below.

TABLE IV

Mixture	Composition	Liquid Transition-ion Point (C°)	Color	Mole Fraction PPMeOB
N	40% Chol.Oleate 50% PPMeOB 10% PPPOB	39.1°	Red	0.85
O	40% Chol.Oleate 45% PPMeOB 15% PPPOB	40.0°	Green	0.81
P	40% Chol.Oleate 30% PPMeOB 30% PPPOB	42.7°	Blue Green	0.54
Q	40% Chol.Oleate 15% PPMeOB 45% PPPOB	45.7°	Blue	0.27

Upon heating of the liquid transisition point, the mixtures N-Q lose color. The compositions M-R exhibit hysteresis properties.

Referring to Figure 2, one may observe the linearity of the graph plotting of the liquid transition points for the compositions of mixtures N-Q. The compositions N-Q are useful as indicating compositions for liquid crystal clinical temperature recorders, useful in medical diagnosis.

The Examples 1-3 show one of the advantages of the compositions of the invention for manufacturing thermal indicating devices. As shown by the examples, the liquid transition point may be controlled directly by the variation of the mole fraction of the nematic type liquid crystal ingredients. It will also be observed that a relatively large change in the mole fraction of the ingredients results in a relatively small shift in liquid transition point, assuring accurate results when the compositions are used as temperature sensing indicators.

Example 4

Following the procedure of *Example 1*, supra., but replacing the cholesteryl oleyl carbonate as used therein with an equal proportion of sitosteryl oleyl carbonate, cholesteryl phenyl carbonate, cholesteryl sebecate, cholesteryl phenylacetate and stigmasteryl oleyl carbonate, respectively, there is obtained a plurality of series of compositions of the invention, useful as temperature indicating compositions.

Example 5

Following the procedure of *Example 1, supra.*, but replacing the PPPOB and PPMeOB as used therein with equal proportions of

4-n-pentylphenyl-4-n-methoxybenzoate
and
4-n-butylphenyl-4-n-heptylbenzoate
or
4-n-hexyloxyphenyl-4-n-butylbenzoate
and
4-n-heptyloxyphenyl-4-n-butylbenzoate

respectively, compositions of the invention are obtained which exhibit hysteresis and which within each series form a linear array of liquid transition points.

The liquid crystal compositions of the invention are particularly useful as the temperature indicating component of a medical or clinical temperature indicating and recording device. Referring now to Figure 3, an isometric view of an embodiment temperature recorder, one may appreciate the utility of the compositions of the invention. In Figure 1, clinical temperature recorder 10 comprises a base or support member 12 including a handle portion 14. End 16 of the support member 12 is designed to be placed in the oral cavity of a patient whose temperature is desired. Disposed on end 16 are a plurality of indicating compositions of the invention. Each of the indicating compositions disposed on end 16 of member 12 are identified by the temperature (in degrees F.) at which the indicating composition will pass through its liquid transisition point. Thus, the liquid crystal composition of the invention disposed on end 16 and identified as "97" will change from its colored mesomorphic phase to a colorless state if the patient's temperature exceeds 97°F. As a further illustration, the liquid crystal composition of the invention disposed on end 16 and identified as "101" will pass from its colored mesomorphic phase to the colorless isotropic liquid phase if the patient's temperature exceeds 101°F. Since the liquid crystal compositions of the invention exhibit hysteresis, i.e.; "memory" when the recorder 10 is withdrawn from the patient's oral cavity, one may readily observe the highest temperature to which the recorder 10 was exposed by viewing the colorless liquid crystal compositions disposed thereon. Hysteresis may be controlled for any desired period up to several hours. In the illustration of Figure 3, the patient's temperature was between 101°F. and 102°F. as indicated by the colorless state of the indicator "101" and those compositions below the "101" indicator.

Support member 12 may be fabricated from any rigid, semi-rigid or flexible support material which is chemically and physically inert towards the indicator compositions disposed thereon. Illustratively, member 12 may be fabricated from paper which is coated with polyethylene or like protective film. Alternatively, member 12 may be fabricated from cellulose acetate, cellulose acetate butyrate, polyvinyl chloride, polyethylene, polyvinyl alcohol, polyvinylpyrrolidone and the like. Preferably support member 12 is of a dark color to absorb light and permit observation of the light scattering effect of the indicator composition.

The indicator compositions may be coated on support member 12, using conventional techniques such as by gravure printing, silk screen printing and like methods. Advantageously the thickness of the coating of the indicator compositions of the invention on member 12 are from about 10 to about 125 microns. The compositions of the invention may be applied directly to the surface of member 12. In such case it is preferably that the coatings of indicator compositions are then protected from the atmosphere and other contaminants by a thin film overlayer 18 as shown in Figures 3 and 4. Overlayer 18 may be any transparent or translucent material immiscible with the indicator composition, for example casein glue, polyvinyl alcohol, polyethylene, methacrylate and the like. The structural details of recorder 10 may be seen further in Figure 4, a cross-sectional side elevation along lines 4-4 of Figure 3. However, it is preferable that the liquid crystal compositions of the invention are first encapsulated and the encapsulated compositions affixed to support member 12 by conventional and known technique. Encapsulated material generally has a longer shelf-life, brighter colors and enhanced stability. The techniques of encapsulation of liquid crystals are generally well known: see U.S. Patent 2,800,457 describing closed core microencapsulation and U.S. Patent 3,341,466 describing macroencapsulation.

WHAT WE CLAIM IS:-

1. A temperature indicating composition comprising in admixture:

a) an optically active cholesteric liquid crystal compound which is chemically inert with respect to other components of the compositions; and

b) a mixture of at least two different nematic liquid crystals having liquid transisition points within 20°C of each other and each being an ester selected from the following:

4-alkylpheny-4-alkoxybenzoates,
4-alkylphenyl-4-alkylbenzoates,
4-alkoxyphenyl-4-alkylbenzoates, and
4-alkoxyphenyl-4-alkoxybenzoates;

the proportion of a) being such that the composition selectively scatters light from the visible spectrum and exhibits a colour at temperatures below the liquid transisition point but which ceases to scatter light from the visible spectrum and becomes colourless at temperatures above the liquid transition point.

2. A composition according to claim 1, wherein the liquid transition point of the composition is in the range 35.9°C to 45.7°C.

3. A composition according to claim 1 or 2, wherein the proportion of a) in the composition is such that the pitch of the composition is in the range 440 to 680μ.

4. A composition according to claim 3, wherein said pitch is in the range 480-600μ.

5. A composition according to any one of claims 1-4, wherein the proportion of a) in the composition is from 25-60% by weight.

6. A composition according to any one of claims 1-5, wherein the liquid transition point of the cholesteric liquid crystal compound is within 20°C of the liquid transition point of the mixture of the nematic liquid crystals.

7. A composition according to any one of claims 1-6, wherein the cholesteric liquid crystal compound is cholesteryl oleyl carbonate.

8. A composition according to claim 7, wherein the proportion of said carbonate is 40% by weight.

9. A composition according to claim 7, wherein the proportion of said carbonate is 50% by weight.

10. A composition according to any one of claims 1-6, wherein the cholesteric liquid crystal compound is cholesteryl oleate.

11. A composition according to claim 10, wherein the proportion of said oleate is 40% by weight.

12. A composition according to any one of the preceding claims, wherein the two nematic liquid crystals are both 4-alkylphenyl-4-alkoxybenzoates.

13. A composition according to claim 12, wherein the two nematic liquid crystals are 4-*n*-pentylphenyl-4-*n*-pentyloxybenzoate and 4-*n*-pentyl-4-methoxybenzoate.

14. A temperature recording device comprising an opaque support and disposed thereon a temperature indicating composition as claimed in any one of the preceding claims.

15. A device according to claim 14, wherein there are disposed on said support at separate locations thereon at least two temperature indicating compositions as claimed in any one of the preceding claims, the two compositions having different liquid transition points.

16. A device according to claim 15, comprising a plurality of such temperature indicating compositions at different locations on the substrate, the different compositions having liquid transition points over the range 97°F to 104°F.

17. A device according to any one of claims 14-16, wherein the temperature indicating composition(s) is or are disposed on a dark support and covered with a transparent or translucent protective film.

18. A device according to any one of claims 14-16, wherein the temperature indicating composition(s) is or are disposed on the support in an encapsulated form.

19. A device according to claim 14, substantially as hereinbefore described with reference to Figures 3 and 4 of the accompanying drawings.

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1583137 COMPLETE SPECIFICATION

3 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 1

FIG. 1

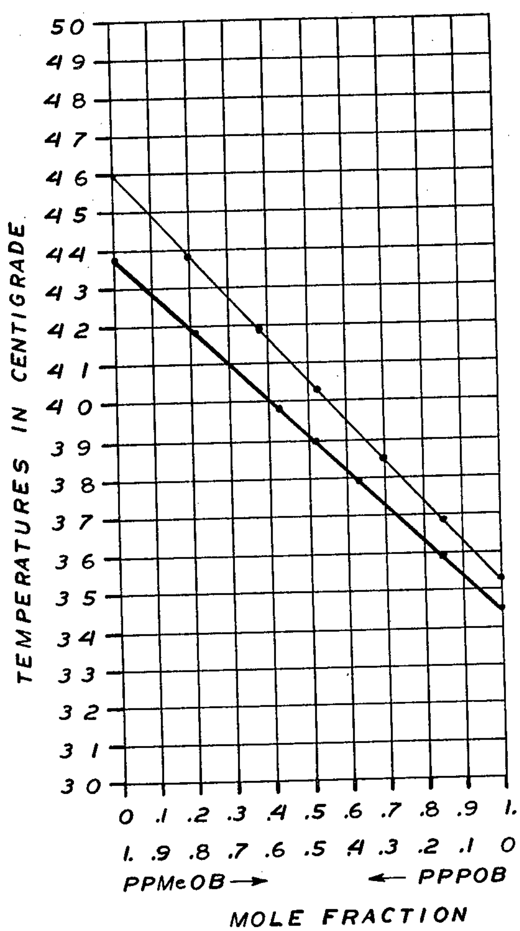
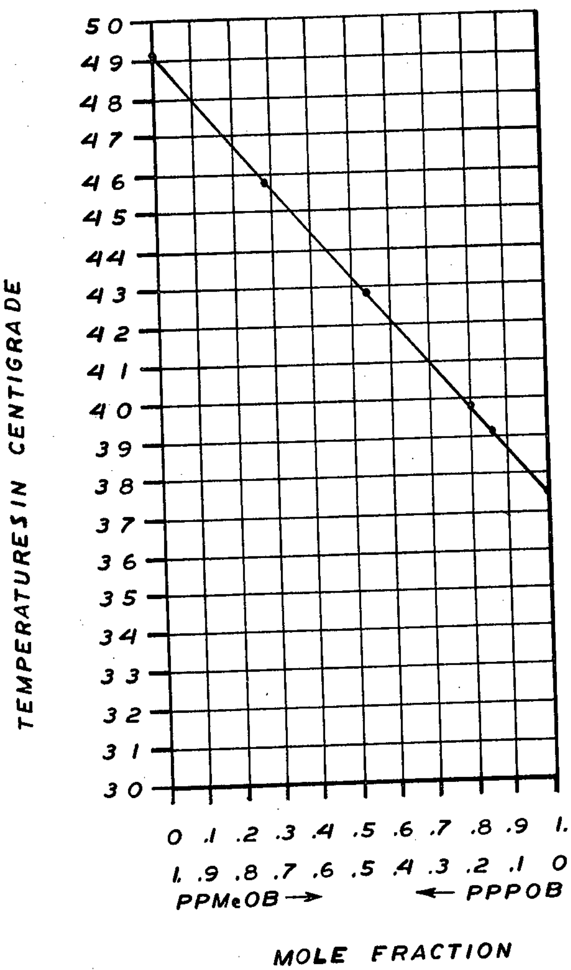


FIG. 2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TEMPERATURES IN CENTIGRADE
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PPMeOB →
← PPPOB
MOLE FRACTION

1583137 COMPLETE SPECIFICATION

3 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 3

FIG. 3

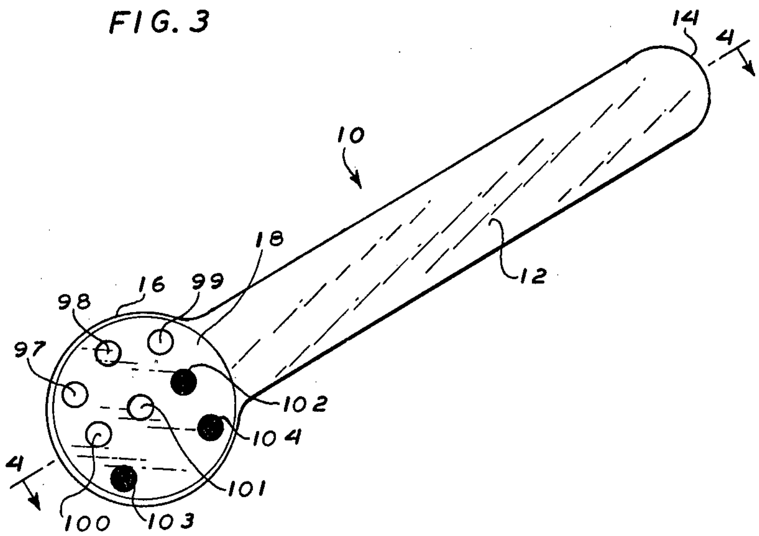

FIG. 4