expected for "random" distribution. After 20% cottonseed oil ingestion the saturated triglycerides were 235% of that expected of "random" distribution.

Whereas in the case of the rats it was necessary to explain a tendency to even distribution of ingested fat, in the case of the chick one must explain a tendency to a directed esterification to form simple triglycerides. Possibly the elevated temperature of the bird can explain the difference. It has been demonstrated that fatty acid activating enzymes have a higher affinity for saturated acids (18, 20). The increased rate of reaction at the higher temperature of the bird may increase the speed of esterification on the 2 and 3 positions of the glycerol sufficiently to account for the small increase in amounts of trisaturated glyceride above that expected by random distribution.

Summary and Conclusions

In order to determine the glyceride structure of a representative mammal and bird, rats and chicks were raised on an essentially fat-free ration, and the percentage of saturated triglycerides in their neutral fat was determined by an isotope dilution procedure.

In order to determine the influence of ingested fat, second groups were fed the fat extracted from the animals in the first group, at the 20% level. Third groups were fed cottonseed oil, which has "even" distribution of its fatty acid. It was found that:

1. The glyceride structure of endogenous rat fat conforms to the "random" type distribution.

2. Ingested fat appears to be digested and resynthesized by the rat according to "even" type distribution, or, at least, in a manner which tends to distribute the fatty acids.

3. Chicks tend to produce simple or "mono-acid" glycerides (8) in which the percentage of trisaturated glycerides is higher than expected for random distribution.

4. It is suggested that the findings can be explained by a selective affinity of the esterifying enzyme system for saturated acids and for the 1-position on the glyceride molecule. In the case of the bird its higher body temperature may increase the speed of the reaction on the 2- and 3-positions of the glycerol sufficiently to account for an increase in tri-saturated glycerides above that required by random distribution.

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The Microscopy of the Liquid Crystalline Neat and Middle Phases of Soaps and Synthetic Detergents[1]

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THE "neat" and "middle" phases are of importance in both the science and the technology of soap systems (3, 5, 36, 46, 48, 54) and have been observed also in synthetic detergents such as the alkyl sulfates (10) and sulfonates (53). Both phases are representative of the "liquid crystalline" state of matter, also variously known by such terms as "mesomorphic," "anisotropic liquid," and "paracrystalline." Specifically, both phases are considered (7, 23, 40, 54) to be of the "smectic" structure in which the molecules, while parallel to each other and disposed in well-defined, parallel sheets of constant thickness, have a lateral arrangement which is unsystematic and liquid-like.[2] The neat and middle phases are both solutions, i.e., of variable water content and may or may not contain electrolyte and other dissolved components. Ordinarily the neat phase, while by no means a mobile liquid, is soft enough to be pumped whereas middle phase, in spite of containing roughly

twice as much water as neat, is of strikingly stiff consistency.[3]

In the present paper are described a) the various aspects or "textures" which the neat and middle phases have been found to exhibit in the polarizing microscope and b) a selection of textures by which each phase can be identified.[4] While this study is primarily descriptive in its present state of development, the presence of systematic differences sufficient for identification of the two phases suggests a fundamental structural distinction between them.

This work was undertaken primarily because of the need for a simple, direct means of identifying these two phases in fundamental phase explorations or in the study of commercial products and processes. The need is particularly acute where the two phases are mixed with each other or with one or more of the other soap phases. While in a few cases considerable experience and judgment are required for successful recognition, the microscopic approach is ordinarily

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[2] Here and elsewhere in the paper, the term "molecule" is used even though the submicroscopic structural units may be larger than molecules. Actually they are at least double molecules, each pair being linked together at the ionic ends.

[3] In this paper we are concerned with the original neat phase of soap boiling operations, not the high-temperature, low-moisture phase once believed (36, 44, 61, 62) to be continuous with kettle neat but since shown to be a separate phase (46, 47, 54, 60). For brevity and because of long-established usage, we will use the simple term "neat" for the phase of commercial interest, in preference to Vold's "soap boiler's neat" (54, 58).

[4] Following G. Friedel (18), the term "texture" is used for microscopic appearance. "Structure" is reserved for molecular arrangement.

simple and in any case offers a combination of directness and general applicability not found in other techniques.

Among other possible methods for recognizing neat and middle phases, the simple macroscopic observation of relative fluidity (11, 24, 44) fails where most mixtures are concerned. X-ray examination (6, 50, 64) is somewhat time-consuming; furthermore x-ray patterns of liquid crystalline phases lack the multiplicity of sharp diffractions so useful in distinguishing crystalline materials. Vapor pressure (45, 59) and dilatometer (46, 62) studies, as well as other such indirect techniques, require a background of data for the particular system under study, a requirement not usually met in many commercial materials which come to hand, or in phase explorations of unfamiliar systems.

The microscopic method, on the other hand, is rapid and applicable to both phase mixtures and isolated samples.

Much of the present subject-matter applies also to such materials as wetting agents and dyes, and to phosphatides and certain other biological substances.

Earlier Work

Neat soap has long been known to the industry[5] as the soap-rich, relatively fluid, end-product of the soap boiling operation whereas middle soap has been known as a distinct phase for almost 30 years (43). Nevertheless published details on the microscopic characteristics of these phases are still relatively meagre, and no generalized method for distinguishing them microscopically has been proposed. This situation may have arisen from a feeling that there is little point in attempting a microscopic distinction between two liquid crystalline phases both of which are "smectic."[6]

For middle soaps of specified composition, photomicrographs corresponding to some five composition-temperature situations have been found.[7] Of these, one (38) shows middle soap droplets in an isotropic matrix while the remainder, except those in Ref. 55a, exhibit the spectacular fanlike aspect generally referred to as "focal conic." It is this texture on which the smectic nature of middle soap has been predicated by previous workers; however, as will be shown, there are other important textures for middle phase.

Published evidence on the microscopic appearance of neat soap of undoubted phase nature and specified composition (32, 41, 56) is even scarcer and less satisfying than for middle soap. Even taken as a whole, this evidence does not furnish a clear or complete concept of the microscopic characteristics of the neat phase.

Other soap photomicrographs, which on the basis of the foregoing published evidence are presumed to correspond to neat and middle soaps, are found elsewhere in the literature, e.g., Refs. 26 and 33 for middle and 27 and 39 for neat. However since the compositions, particularly water content, are not sufficiently defined, these photographs cannot by themselves be used to establish the microscopic appearance of the two phases.

Also not included in the above summary of published photomicrographs of neat soap are several[8] involving the low-moisture, high-temperature "neat"-phase already referred to in the introduction, and others[9] involving soaps of several percentage moisture in locations where continuity with soap boiler's neat is still an open question. The "superneat" phase (54), whose existence is still questionable (9), falls in the latter category.

Experimental Results and Discussion

I. *Description and Classification of Textures.* The present section consists of a description and a classification of the microscopic textures observed in the neat and middle phases along with the necessary amplifying discussion. Appropriate reference is made to illustrative photomicrographs; in these, unless otherwise noted, the effects are those observed between "crossed" nicol prisms (x-nicols). (The main discussion of phase identification will be found in Section II.)

Table I is a compilation of all microscopic textures so far observed in the neat and middle phases. Asterisks indicate the more common textures. The decimal notation, in addition to indicating the relationships, provides a convenient designation for those textures for which there is no concise word-description. The table not only serves as a key to the descriptive matter in the text but also shows at a glance which textures are exhibited by only one of the two phases, an important point for purposes of identification. Significant absences are a) non-geometric textures in the neat phase, b) "negative" units and, for practical purposes, c) axial textures in the middle phase.

As far as possible the classification is based on fundamental textural distinctions. However certain closely related textures are given separate status because of a) the emphasis on phase identification and b) the existence of considerable differences in appearance between certain related textures, e.g., the fanlike (222.5) and angular (222.6) textures in the middle phase.

There are several reasons for the detail of the present classification. The first is to provide for those occasional phase identifications which require careful attention to textural details and an adequate understanding of the relationships between textures. Another is to provide a basis for distinguishing in the future between the neat and middle phases on the one hand, and certain other mesomorphic soap phases known but as yet inadequately studied; conversely, it is hoped that acquaintance with the present variety of textures will minimize any tendency to attribute each variation in microscopic appearance to a "new phase." Finally it is expected that the detailed classification will contribute to future interpretations of the structures of these phases.

To afford a link with the previous literature, some of the accompanying photomicrographs are of compositions already known to exist as neat or middle soap. The neat soaps are those of potassium oleate [Figures 1, 5, 11-12; cf. McBain and Elford (40)], potassium laurate [Figure 15, cf. McBain and Field (42)], sodium oleate [Figures 13-14, cf. Vold (54)], and a typical commercial soap (Figure 16). The middle soaps are those of potassium laurate [Figures 17, 18, cf. McBain and Field (42)], potassium oleate [Figure 20, cf. McBain and Elford (40)], and sodium palmitate [Figure 23, cf. McBain and Langdon (43)]. For the remaining textures the best available illustrative photomicrographs happen to be of compositions whose phase nature has not previously been reported.

THE NEAT PHASE (100)

110. *Uniaxial Textures.* The designation "uniaxial" covers all textures, smectic and otherwise, in which the detergent molecules[2] are parallel to a common axis; the axis of the structure is also an optic axis, i.e., an optically isotropic direction. When it is a smectic phase which exhibits a uniaxial texture, the parallelism of the molecules is associated with planarity of the smectic sheets, hence the present use of the term *planar.* Planar arrangement is encountered at one time or another in most smectic substances.[10]

[5]See, for example, Refs. 5 and 31.

[6]It is true that Vold (9, 54) has cited examples suggesting that there may be systematic microscopic differences between the various liquid crystalline soap phases; however he did not claim to have done the detailed work necessary to establish such distinctions.

[7]*Potassium laurate:* Compositions ranging 37.5-42% in water, at and above room temperature (34, 35, 37, 38, 49). (For evidence on the phase nature of these compositions, see Ref. 42.)
Sodium oleate: 36% in water, 80° and 115°C. (55).

[8]For example, Refs. 61 and 63.

[9]For example, Ref. 57.

[10]See, for example, Ref. 16.

TABLE I

Classification of Microscopic Textures Observed in the Neat and Middle Phases

100. NEAT PHASE	200. MIDDLE PHASE

110. *Uniaxial* (specif. *Planar*)
   111. Entirely "isotropic" field
      111.1. In homogeneous neat
      111.2. In neat plus an isotropic phase (Figure 9)
   112. Planar matrix for "oily streaks," etc. (Figures 1, 4, 11, 13)[a]
   113. Planar portions of droplets
      113.1. Centers of flattened droplets (Figure 6)[a]
      113.2. Plateaus in terraced drops
	210. *Axial*
	     (Rare)

120. *Focal Conic*
   121. Unit textures
      121.1. Positive units (Figure 1)[a]
      121.2. Negative units (Figure 2)[a]
      121.3. Fanlike units (Figure 3)[a]
   122. Composite textures
      122.1. Mosaic [network of (+) and (−) units] (Figures 4, 5, 12)[a]
      122.2. "Oily streaks" (Figure 11)[a]
      122.3. Birefringent borders (Figures 6, 7)[a]
      122.4. Terraces
      122.5. Fanlike texture (Figure 8)
      122.6. ── ──
      122.7. ── ──
      122.8. Batonnets
	220. *Focal Conic*
	   221. Unit textures
	      221.1. ── ──
	      221.2. ── ──
	      221.3. Fanlike units (Figure 17)[a]
	   222. Composite textures
	      222.1. ── ──
	      222.2. "Oily streaks" (Figure 22)
	      222.3. ── ──
	      222.4. ── ──
	      222.5. Fanlike texture (Figure 18)[a]
	      222.6. Angular texture (Figure 19)[a]
	      222.7. Fields of almost uniform extinction (Figure 20)[a]
	      222.8. Batonnets (Figure 21)

130. *Non-geometric*
     (None)
	230. *Non-geometric*
	   231. Simple (non-striated) (Figure 23)[a]
	   232. Striated
	      232.1. Slip-lines
	      232.2. Incipient geometric texture (Figure 24)[a]

[a] = common textures.

In the neat phase the plane layers have always been found parallel to the surface of the slide even though in certain other substances the layers may not be parallel to the surface (17). Since their optic axis is parallel to the axis of the microscope, any planar areas in the neat phase *appear* to be isotropic when examined between x-nicols in axial (non-convergent) light; with oblique or convergent light however the birefringence associated with directions other than the optic axis is revealed (see Figure 9). In addition, a uniaxial interference figure (Figure 10a) is obtainable from a planar area, thus further demonstrating its anisotropic nature,[11] and justifying the designation of this texture as uniaxial.

Particularly in the more fluid neat soaps, planar areas often form spontaneously from the non-planar textures as a result of the strong tendency of the neat phase to assume its maximum degree of orderliness. Planar areas can also be produced artificially by gentle manipulation of the cover glass, but with more vigorous motions the complex "mosaic" texture results (see 122.1 and Figures 11-12).

Several planar textures are illustrated in Figures 1, 4, 6, 9, and 11. The classical "terraced drops" ("gouttes à gradins") (113.2) are discussed and illustrated by Friedel (12), hence not illustrated here.

120. *Focal Conical Textures*. The focal conic arrangement is the consequence of forces which prevent attainment of the uniaxial planar arrangement. For example, focal conic textures are encouraged by rapid precipitation, mechanical or thermal disturbance, or curvature of the surface of the drop. The smectic sheets are curved and fit "Dupin cyclides," a family of equidistant surfaces based on an ellipse and one branch of a hyperbola located in mutually perpendicular planes and each passing through the focus of the other. For curved smectic sheets this is a configuration of minimum strain (2). Such focal conic structure as it bears on microscopic textures has

been amply described by several writers (2, 3, 13, 19, 25, 28).

Actually, except for Texture 121.1, neither the neat nor the middle phase exhibits focal conic textures in which the ellipses or hyperbolas are obvious. However oily streaks (122.2, 222.2), birefringent terraces (122.4), batonnets (122.8, 222.8) and the fanlike texture (122.5, 222.5) are types specifically recognized by Friedel as usually exhibiting focal conic texture too fine to be obvious; furthermore the character of the remaining textures here classified as focal conic is consistent with focal conic geometry.

It will be seen from the present variety of microscopic appearances all based on focal conic geometry that the simple term "focal conic," as used at times in the soap literature, is really an insufficient description of microscopic appearance.

In our microscopic study of the neat and middle phases it has proven helpful to subdivide the focal conic textures into two principal types: a) the "unit" textures (121 and 221) and b) the composite textures (122 and 222) formed by combining the basic units in various ways. The uniaxial planar textures may be combined with either of these two broad types.

121. The *unit textures* may be encountered either individually or as the units which make up composite textures. It should be stated however that the units are not necessarily structurally identical with Friedel's "focal domain" (13); "unit" is used in a relative sense to describe microscopic appearance and to provide a device for understanding the more complicated textures. As a matter of fact, there are occasions, to be pointed out, when certain of the unit textures exhibit a microscopic fine structure.

121.1. The *positive unit* of the neat phase (Figure 1) takes its name from the fact that its extinction cross exhibits a positive "optic sign."[12] It is further characterized by extinction arms which are narrowest at the center of the cross and which remain parallel to the eyepiece crosshairs as the microscope stage is

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[11] In the soap industry, isotropic liquid phases are of two kinds: a) "Nigre," an old soap-boiling term, refers to solutions relatively rich in soap—a couple per cent or more—and with or without electrolyte, glycerine, and other constituents. b) "Lye" or "seat" refers to a relatively soap-free phase of several per cent electrolyte content.

[12] The "optic sign" is determined by considering the extinction cross as if it were a uniaxial "interference figure" and proceeding as in optical crystallography. "Positive" corresponds to a *radial*, and "negative" to a *tangential*, vibration direction for the component of higher refractive index.

rotated. In addition, one of the extinction arms becomes curved if the sample is tilted around that arm as an axis. Since such tilting from the horizontal is not one of the common operations of microscopy, it is fortunate that this third criterion, once established, is not needed in phase identification.

There is however a structural reason for imposing it, for thereby the designation "positive unit" is reserved for a textural type which is actuallay an individual focal domain (13). The positive unit is the only one of the neat or middle textures in which one of the fundamental focal conics is obvious: positive units, whenever separate, appear as circles and, when in composite textures, occasionally have a distinct elliptical outline. Each positive unit constitutes a focal domain viewed normal to its elliptical base. In the neat phase all separate, and the great majority of combined, positive units represent the special case in which the ellipse is a circle and the hyperbola is a straight line normal to this circular base. For all such units the extinction arms are straight and the extinction cross therefore is plus-shaped.

In the comparatively rare case in which the base is actually an ellipse, one of the extinction arms is curved, the other straight, in analogy to the tilting behavior noted above. This behavior, incidentally, proves that the positive unit, while circular as commonly viewed, is not centrosymmetrical in three dimensions.

A further feature of separate positive units is that their circular bases are always on the top or bottom surface of the preparation (Figure 1). From the established relationship of the actual molecules to focal conic geometry (3), it follows that in the base of each positive unit the molecules are arranged radially. Therefore, when the extraordinary ray of the aggregate is operating, there should be an abrupt optical discontinuity at the interface between the unit and the planar matrix; this is actually the case.

The true positive unit, as above defined, is found only in the homogeneous neat phase, specifically as an individual unit embedded in a planar matrix (Figures 1, 4) or as a component of one of the composite textures. [In 2-phase systems, neat droplets of positive sign (Figure 3) are common, but actually these are fanlike units (121.3).]

121.2. The *negative unit*, by analogy with the positive unit, exhibits a negative optic sign.[12] In further contrast to the positive unit, the negative extinction cross possesses arms which are broadest at their intersection (Figure 2a). In addition, on rotation of the microscope stage, the negative cross does not remain plus-shaped. Instead it distorts into a sort of "pinwheel," fully developed (Figures 2b, 7b) after 22.5° rotation from the plus-position; after 45° rotation the unit appears as a quatrefoil or, for elongated negative units, a figure 8 (Figure 7c). The contrasting behavior of positive and negative crosses is shown in very simple form in one of the droplets of Figure 3.

Actually the extinction cross of a negative unit is an artifact since examination at higher powers shows the two arms to lie at different levels. However since the negative units are so common and characteristic and since their complex character gives no difficulty at ordinary magnifications, it is helpful to treat them as an entity in the study of the neat phase textures. Structurally, the negative unit results from the fact that the vertices of adjacent positive units are alter-

nately on top and bottom surfaces of the preparation.

121.3. The *fanlike unit*, along with oily streaks (122.2, 222.2), batonnets (122.8, 222.8), and the composite fanlike texture (122.5, 222.5), is specifically described by Friedel as being focal conic (14). While it superficially resembles the positive unit in exhibiting a positive sign and an extinction cross with narrow center and straight arms (Figure 3), it is not a single focal domain. At times the complex character of the fanlike unit is evident as a distinct ribbed appearance (Figure 8) and a scalloped border (Figures 3, 8). In certain cases (Figure 8) this border is seen to consist of chains of negative units. At other times there is no immediate evidence of the complexity. However when necessary, a suspected fanlike unit has been identified by tilting from the horizontal; unlike the positive unit, its extinction arms remain straight.

A common fanlike unit is the rounded droplet (Figure 17), which often results on slow precipitation from isotropic liquid. The droplet may be anything from a full 360° fan exhibiting a complete extinction cross to, at the other extreme, a sector far from the (imaginary) center of its fan; in the latter type of droplet all molecules are essentially parallel and the drop exhibits almost uniform extinction.

Neat phase at times exhibits these rounded droplets which are actually more common in middle phase. While neat phase in this guise can usually be identified satisfactorily with the help of other textures in the same preparation, and while ordinarily such droplets in neat are considerably smaller than in middle, the existence of such a texture in neat must be recognized in order to avoid careless identification as middle phase.

122. While the simple textures are fairly common, it is the composite textures, especially the "mosaic" texture (122.1) and the "oily streaks" (122.2), which are present or producible in almost any neat phase preparation. These composite textures are somewhat analogous to a polycrystalline region in a fully crystalline material. However, whereas the latter involves actual discontinuities between "grains" at their boundaries, the neat phase exhibits a continuous gradation from one unit to the next, an occurrence permitted by distortion of the smectic layers. The geometry of a typical gradation is well illustrated in Figure 4. This textural gradation is a fundamental basis for distinguishing neat from middle phase, which does exhibit discontinuities at its "grain" boundaries.

122.1. The mosaic texture, a network of (+) and (−) units, is the first composite texture considered because, modified to a greater or less degree, such a network is evident in all the succeeding neat textures. In the unusually coarse mosaic of Figure 4 the sharing of extinction arms between adjoining positive and negative crosses can be seen; it will also be noted that the negative crosses, being broader at the center, are more prominent.

Ordinarily such networks are much finer than in Figure 4, giving rise to the characteristic appearance (Figures 5, 12) which originally suggested the term "mosaic." It is not only a common but also an important identifying texture for the neat phase. It is rarely so fine-grained that some of the negative units cannot be observed to pass through the pinwheel aspect as the stage is rotated.

Study of an unusually well developed example of mosaic texture at about $500\times$ has shown that the appearance results from the presence of the "polygonal structure" described in some detail by Bragg (4). The positive units of the mosaic are Bragg's pyramids with polygonal bases. The mosaic network arises from alternation of base-up and base-down pyramids, with the complex zone between pyramids giving rise to the extinction pattern designated here as "negative unit." At $500\times$ it is possible to focus separately on top-level and bottom-level polygons, but with intermediate focus the preparation shows the typical mosaic texture exhibited at lower power or in the more common mosaics which are too fine to show the polygonal structure.

The transformation of planar areas into fine mosaic texture when sufficiently disturbed mechanically (Figures 11-12) or thermally (Figures 13-14) is a highly characteristic property of the neat phase. Both these effects are often spontaneously, though sometimes slowly, reversible on removing the mechanical disturbance or on cooling, especially once the birefringent network is broken at some point. Conversion into the mosaic texture, either mechanically or thermally, is an important means of distinguishing a planar neat area from truly isotropic liquid.

The mosaic texture is actually the maximum degree of microscopic disorder possible in the neat phase, i.e., the opposite extreme from the planar arrangement. After a severe disturbance, sufficient to destroy any geometric pattern in a more rigid material such as a microcrystalline aggregate or the middle phase, the fluidity of the neat phase (and probably also its structure, see Section III) permits it to adjust immediately into the fine focal conic texture here termed "mosaic." On the other hand, unlike the middle phase, mosaic neat phase does not usually show any tendency toward spontaneous coarsening of its texture (see Figure 5) even in the presence of mother liquor (cf. footnote 13).

Inspection of Photograph I of McBain and Elford (40) (potassium oleate neat soap) reveals crosses of the negative type, establishing the mosaic nature of the texture. A corresponding area in cholesterol butyrate is found in Plate 28 of Friedel's treatise (13) and is there designated "fine, fanlike, birefringent areas (conic)."

122.2. "Oily streaks" (Lehmann's "ölige streifen," Friedel's "stries huileuses"), in addition to being one of the earliest observed textures in liquid crystals generally (29) and in liquid crystals of soaps (30), are ordinarily encountered in a freshly pressed-out sample of homogeneous neat phase (Fig. 11). They evidently arise from stirring the mass or from other similar causes of linear orientation. For example, an oily streak is observed to form in the wake of an air-bubble passing across a planar area. The reverse process, because of the tendency of molecules to assume the planar arrangement, occurs quite promptly if the oily streak breaks at any point. Generally however, the oily streaks are more stable than any mosaic texture which may be formed by deformation of the preparation.

Oily streaks ordinarily exhibit a fine cross-banding though occasionally a coarser, focal conic texture like that illustrated in Figure 7 is encountered. In spite of such detail however the over-all extinction is paral-

lel and the "elongation" negative, i.e., the higher-index component vibrates crosswise.

122.5. Composite fanlike texture is the type of focal conic variation designated "fan structure" ("structure en éventails") by Friedel (14). According to Friedel, the fan is a composite of focal domains whose hyperbolas are so elongated that they appear as a group of straight lines converging from their respective focal regions to a common point; the focal conic geometry, if visible at all, would thus be sought at the outer edge of each sector of the fan. The positive "sign of elongation" of the sectors of the fans indicates a lengthwise molecular alignment in Friedel's interpretation of the texture. In both neat and middle phases this texture is favored by slow precipitation from isotropic mother liquor.

The texture is not too common in the neat phase; however it is another texture whose existence must be recognized because of the possibility of confusion with a very common texture of middle phase. In neat phase the fanlike texture has always been found in close association with a few negative units (see Figure 8), which serve to distinguish such neat from fan-like middle phase. Furthermore there is often a scalloped appearance at the outer edge of the fan, resulting in local curvature of the extinction arm; also, wherever a fan intersects another focal conic area there is no discontinuity as in middle phase, but a merger of the two zones. This texture, like rounded droplets (see under 121.3), is considerably finer than the corresponding one for middle phase.

122.8. "Batonnets" are a type of pointed droplet exhibited by smectic substances (15). Since they are usually associated with rapid precipitation, they are rather commonly encountered in neat phase precipitated from isotropic liquid by cooling or by evaporation near the edges of the cover glass. The presence of batonnets in neat phase precipitating from isotropic liquid in 56.5% potassium oleate at $240°C$. was one of the properties used by McBain and Elford (40) in characterizing neat soap as smectic.

THE MIDDLE PHASE (200)

Like the neat phase, the middle phase exhibits axial (210) and focal conic (220) textures;[13] unlike neat, middle exhibits a group of non-geometric textures (230).

210. Axial Textures. These textures are analogous to the uniaxial textures in neat (see 110) and likewise involve a planar arrangement; however for lack of specific evidence the term uniaxial is not applied to the middle phase. True planar textures in middle phase are rare. The only example so far observed here has been in 45% potassium laurate (55% water), cooled from the isotropic phase and held several minutes at $161°C$. just below T_i, the highest temperature at which the liquid crystalline phase is in equilibrium with isotropic melt.

220. Focal Conic Textures. (See general comments, Section 120.)

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[13]Middle phase, if at all capable of developing geometric texture, ordinarily develops relatively coarse patterns simply on spontaneous digestion. It has been noted that the development of geometric texture occurs only in the presence of visible isotropic liquid or near the middle-plus-nigre portion of the system, i.e., on sufficient dilution or heating. This may mean either that some isotropic liquid is required for development of the middle phase "grains" by digestion or that the middle phase proper, when sufficiently hydrated or heated, becomes fluid enough to permit its rearrangement into geometric textures. Reference to the appropriate phase diagram (42, 54) shows that all compositions for which geometric middle soap textures have been published (see earlier work) lie close to the nigre region.
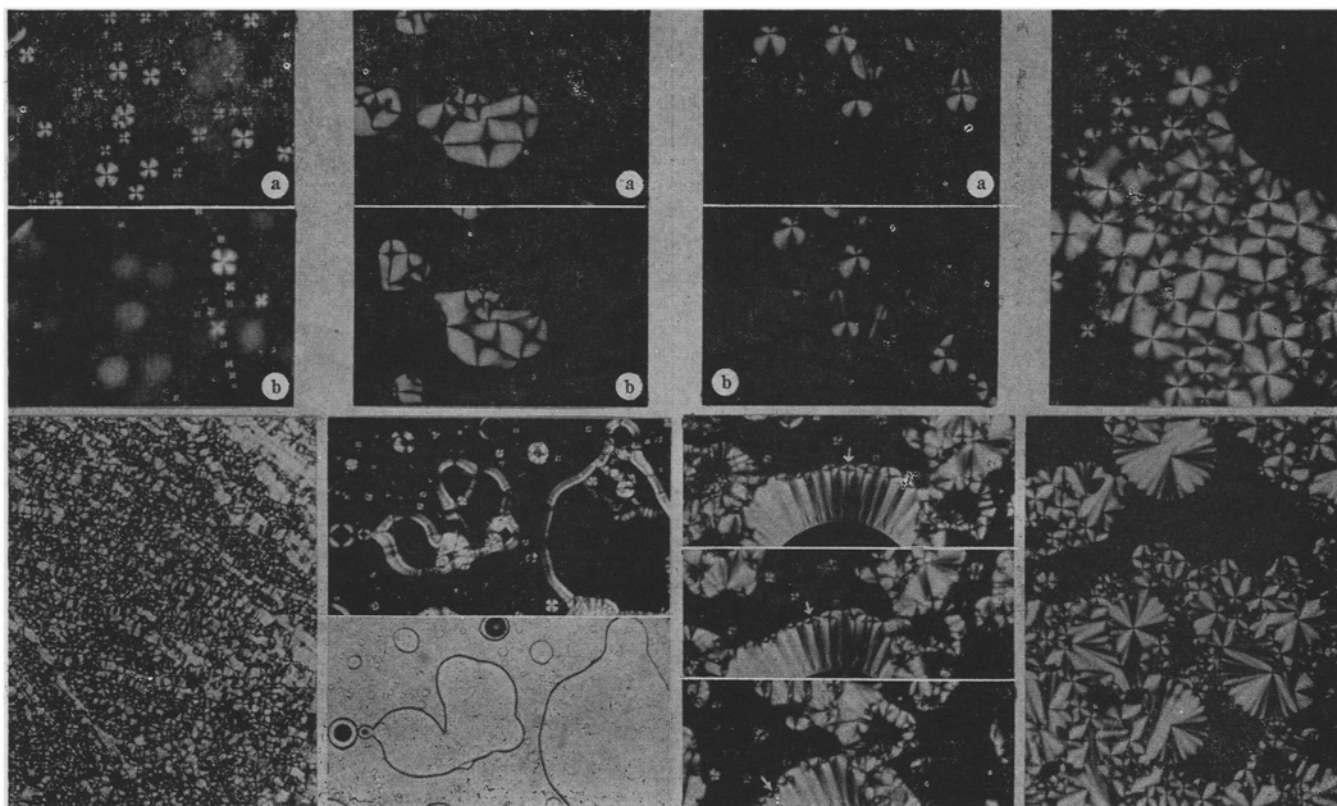
FIGS. 1-8: FOCAL CONIC TEXTURES OF NEAT PHASE
(With x-nicols except Fig. 6b; Fig. 4-5 magnif. ca. 100×, others ca. 200×)

FIG. 1. *Positive units* (121.1) in *planar uniaxial matrix* (112); focussed successively on (a) top and (b) bottom surface of preparation. Note narrow center of extinction crosses. Potassium oleate, ca. 30% water, (ca. 7 Nw, cf. Ref. 40).

FIG. 2. Near center of field, *negative units* (121.2) in matrix of isotropic phase. In a, crosses are plus signs, broadened at the center; in b, where the stage has been rotated 20-25° clockwise, the extinction arms are curved, resulting in the "pinwheel" aspect.

FIG. 3. *Fanlike units* (121.3) of neat in nigre, with superficial resemblance to true positive units. Note the narrow-centered extinction crosses whose arms remain straight in spite of rotation of the stage 20-25° clockwise in b, and the scalloped edges. Also note, near the right-hand border, the droplet consisting of one negative and one fanlike unit.

FIG. 4. Coarse *mosaic texture* (122.1), a complex network of (+) and (−) units. Note how arms of crosses are shared by adjacent units of opposite sign and how negative crosses are more prominent. (In upper left, *positive units* in *planar matrix*.)

FIG. 5. Typical *mosaic texture* (122.1); same geometry as in Fig. 4, but finer and less regular. (Present sample is homogeneous neat phase which showed no textural growth or other change over 3-month period.) Potassium oleate, 30% water, room temp.

FIG. 6. Large, flat, neat droplets in isotropic liquid, with and without x-nicols. Note *birefringent borders* (122.3) where curvature of the surfaces is considerable, also *planar centers* (113.1). Note, also, the extreme difference in contrast in b between outer and inner edges of borders. (Black centers of two circular drops in b are air bubbles.)

FIG. 7. Focal conic detail in *birefringent border* (122.3) adjoining air bubble. Arrow indicates progression of negative unit to pinwheel and then to Figure 8 as stage is rotated counterclockwise (cf. Fig. 2).

FIG. 8. *Fanlike texture* (122.5); neat droplets in isotropic liquid. Note the several pinwheels which distinguish this from the fanlike texture of middle phase.

221. (cf. 121.) Only one unit texture is encountered, the fanlike unit. With positive units absent, the middle phase exhibits no simple focal conic geometry. Since negative units do not occur, the resulting absence of curved extinction arms is of fundamental importance in distinguishing this phase from neat.

The absence of negative units in the middle phase arises from the fact that adjoining fanlike units do not merge with each other, as do adjacent units of the neat phase; instead they meet along an ordinarily irregular boundary like those in a typical polycrystalline aggregate.

221.3. (See 121.3.) Separate fanlike units are found among the rounded droplets (Figure 17) which the middle phase precipitates by evaporation of water from an isotropic solution. The texture is that shown by McBain in Ref. 38. Further growth of such drops by cooling or by evaporation of water leads ultimately to a composite fanlike texture.

222. It will be noted in Table I that the most common composite textures of the middle phase are relatively uncommon in a neat and vice versa.

222.2. In the middle phase, unlike the neat phase, oily streaks (Figure 22) are encountered only in a matrix of isotropic phase, evidently because the localized flow required for generation of this texture is not possible with the high viscosity of the homogeneous middle phase.

222.5. The spectacular fanlike texture (Figure 18, see 122.5) is the one most commonly associated with middle phase (34, 37, 54). In this phase, focal conic detail in the fans is ordinarily invisible though at higher powers (ca. 500×) there is sometimes a suggestion of it; the fineness of the ribs indicates that the fan is made up of many narrow domains whose terminal detail would necessarily be very fine. The boundary betwen two fanlike areas is a sharp discontinuity, apparently consisting only of the irregular line along which two adjacent liquid crystalline zones
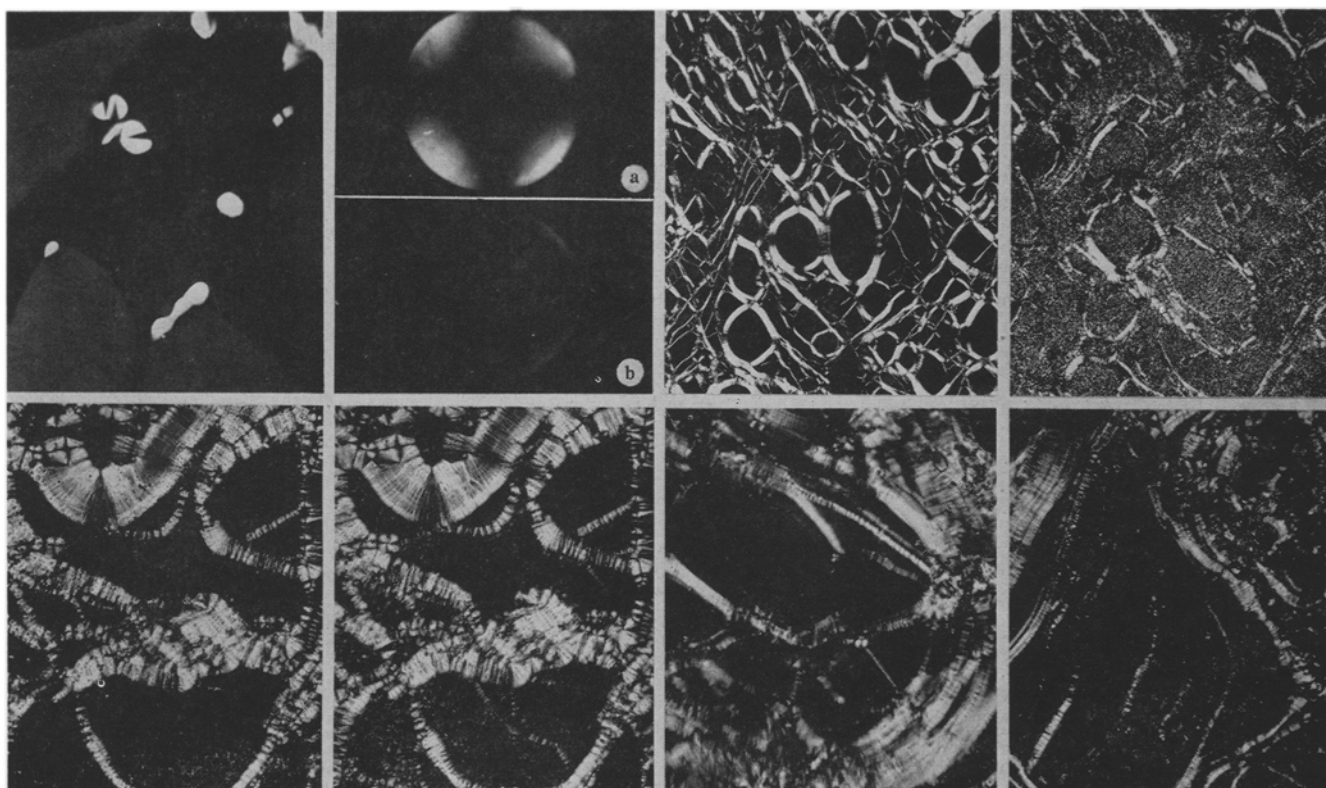
FIGS. 9-16: ADDITIONAL TEXTURES OF NEAT PHASE
(All with x-nicols)

FIG. 9. *Planar* neat phase (gray) distinguished from isotropic liquid (black) using convergent light. (Bright drops are middle phase.) With axial light, the neat and isotropic liquid were indistinguishably black (texture 111.2). Magnif. *ca.* 100×.

FIG. 10. (a) Uniaxial interference figure on thick planar droplet of neat phase (as in Figure 6). (b) Blank on truly isotropic phase in same field.

FIG. 11. *Oily streaks* (122.2) in *planar matrix* (112). Potassium oleate, 30% water, room temperature. Magnif. *ca.* 50×.

FIG. 12. Field of Fig. 11 after mechanical disturbance of cover glass. In spite of unavoidable distortion with such fluid material, conversion of certain planar patches to the mosaic texture (122.1) can be followed.

FIG. 13. Homogeneous neat phase at 50°C.; *oily streaks* in *planar matrix*. Sodium oleate, 32% H_2O. Sample in sealed, flat, glass capillary. Magnif. *ca.* 100×.

FIG. 14. Field of Figure 13 after heating to 150°C. Note thermal conversion of planar patches to mosaic texture (122.1).

FIG. 15. Neat phase of potassium laurate, 20% H_2O (16.8 N_w; *cf.* Ref. 42), *ca.* 60°C. Magnif. *ca.* 100×.

FIG. 16. Neat phase in typical commercial "kettle soap." Sodium soap of 80% tallow–20% coconut oil. "Framed" soap at 30% water, remelted on slide. Magnif. *ca.* 100×.

happen to meet and stop growing. The extinction arms of a middle phase fan, from the apex to this outer boundary, are straight.

222.6. The "angular" texture (Figure 19) often exhibited by middle phase is really an underdeveloped fanlike texture. Apparently because there are many "grains" in close proximity, the development of obvious fans is restricted though at least a few small fans are usually found; the majority of grains are angular fragments of fans. The angular texture is likely to be encountered in digested middle-plus-nigre systems. On longer digestion, this texture often develops gradually into the large, almost homogeneous fields of 222.7.

An angular texture in the smectic phase of the soap-like bromphenanthrene sulfonic acid is found in Ref. 51.

222.7. (See Figure 20 and discussion under 222.6.)

222.8. *Batonnets.* (See Figure 21 and notes under 122.8.)

230. *Non-Geometric Textures.* In addition to the foregoing textures, all of which are characterized by more or less geometric design, there is in the middle phase an important and common type of texture that exhibits no definite geometry though the birefringent character is evident. It is particularly important to recognize the existence of these textures because of the emphasis laid by the previous literature on the geometric textures, especially fanlike textures.

231. The *simple, non-striated* type of non-geometric middle phase texture is illustrated in Figure 23. Rather nebulous patches, arising from more or less parallel orientation of submicroscopic birefringent units, are evident and exhibit a crude extinction as the microscope stage is rotated. An identical texture is exhibited between x-nicols by a paste of fine-microscopic, or submicroscopic, elongated crystals, but in such a case the mass is ordinarily opaque both in bulk and microscopically and would not be mistaken for the clear middle phase.

This particular non-geometric texture of the middle phase is believed to be stable only in the absence of mother liquor.[13]

232. *Striated,* but otherwise non-geometric, textures appear to have one of the following two modes of origin.

232.1. Striations develop as slip-lines in stiff, homogeneous middle phase. On standing, no further change in texture occurs.

FIGS. 17-24: TEXTURES OF MIDDLE PHASE
(x-nicols)

FIG. 17. *Fanlike units* (221.3) of middle phase; rounded droplets precipitated under cover glass on slow evaporation of water from 20% aqueous solution of potassium laurate; room temperature. Magnif. *ca.* 100×.

FIG. 18. *Fanlike texture* (222.5). Note straight extinction arms and absence of "pinwheels." Potassium laurate; middle phase precipitated as in Fig. 17. Magnif. *ca.* 50×.

FIG. 19. *"Angular" texture* (222.6). Note absence of "pinwheels." Magnif. *ca.* 50×.

FIG. 20. *Zone of almost uniform extinction* (222.7). Middle phase precipitated as in Figure 17 but starting with potassium oleate in 20% solution. In *a*, sample at extinction; in *b*, sample at maximum brightness (by turning nicols rather than sample 45°). Magnif. *ca.* 25×.

FIG. 21. *Batonnets* (222.8) of middle phase precipitating from isotropic liquid. Magnif. *ca.* 50×.

FIG. 22. *"Oily streaks"* (222.2) of middle in isotropic liquid. Magnif. *ca.* 200×.

FIG. 23. *Simple non-geometric texture,* non-striated (231), in homogeneous middle phase. 30% sodium palmitate, 70% water, 80°C. (*ca.* 1.5 N$_w$; *cf.* Ref. 43). Magnif. *ca.* 100×.

FIG. 24. *Striations* in incipient geometric texture (232.2) in middle phase. Magnif. *ca.* 50×.

232.2. More commonly, the striations represent incipient development (Figure 24) of the angular or fanlike textures.

II. *Microscopic Identification of the Neat and Middle Phases.* Ordinarily, distinguishing between neat and middle phases microscopically is simply a matter of inspecting a preparation for the more common textures indicated in Table I. For convenience however, and to provide for those occasions where the two phases cannot be distinguished without attention to textural details, the distinguishing textures and textural interconversions are summarized in Table II, which is the heart of the present section.

With respect to identification, one helpful feature of the situation is that the textures in which neat and middle phases most resemble each other are usually associated with quite different conditions. Therefore, in any mixture of two or more phases, a type of situation where the microscopic method is particularly needed, neat and middle would be expected to exhibit quite different aspects and be readily distinguishable. Under such conditions, furthermore, since the phases exist side by side, valid comparisons of birefringence can be made (see below).

In any case, of course, it is advisable to base the microscopic identification of these phases on a combination of textures.

A warning needs be given regarding dependence on birefringence, *i.e.*, strength of double refraction, as an identifying property. This property is ordinarily used as a preliminary and tentative test. While it is true that each of the non-planar textures displays, somewhere in a preparation, regions where the molecules lie parallel to the surface of the slide and more or less parallel to each other, thus exhibiting substantially the maximum birefringence, nevertheless the interference "color" observed depends partly on thickness of the area, which varies from slide to slide and often from one side to the other of a given preparation. However where the two phases exist side by side, reliance can be placed on a difference in birefringence.

Another property of occasional value is the contrast between the neat or middle phase and its surroundings; this property, dependent on relative refractive indices of the phases forming the interface, is therefore related to birefringence, as just discussed. With the analyzer out, the difference in index between neat phase, even planar drops, and a separate isotropic phase ordinarily leads to good contrast at the interface (Figure 6a); on the contrary, patches of middle phase in an isotropic liquid matrix are often practically invisible without x-nicols, since even the highest index of middle phase is little different from that of the mother liquor. Even where oily streaks or other neat phase structures are embedded in an isotropic matrix of the same phase, there is fairly good contrast at the boundaries, especially if the stage is turned to the position where the higher refractive index of the neat is oper-
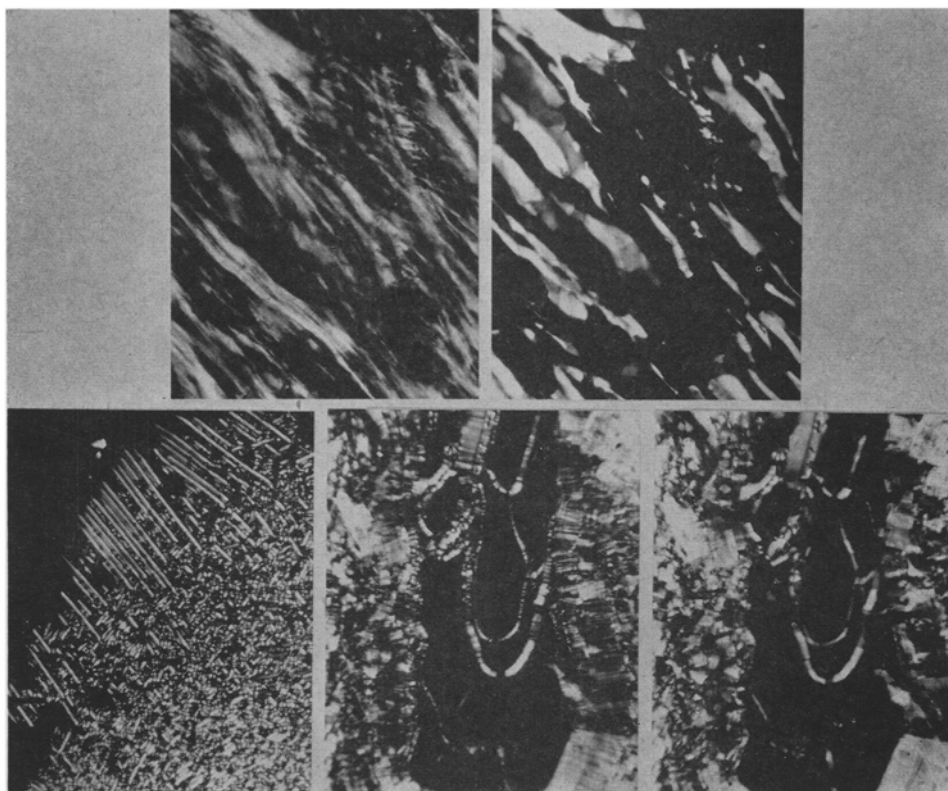
FIGS. 25-29: THE "VISCOUS NEAT" CONDITION

(x-nicols)

FIG. 25. "Viscous neat" freshly pressed out under cover glass. Potash soybean soap, *ca.* 40% water, room temperature. Magnif. *ca.* 100×.

FIG. 26. Field of Figure 25 after 100 min. Note considerable conversion to planar uniaxial texture.

FIG. 27. Angular mosaic texture obtained by disturbing planar area in "viscous neat." Potash soybean soap as in Figure 25. Magnif. *ca.* 100×.

FIG. 28. Neat phase in potash soybean soap, 40% water, *ca.* 50°C. Note typical fine crossbanding and rounded contours. Magnif. *ca.* 50×.

FIG. 29. "Viscous neat" after cooling field of Figure 28 to room temperature. Note angular jointed oily streaks and absence of fine banding.

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ative. Because of the dependence of refractive index on composition however, and the dependence of contrast on thickness of the region and curvature of the interface, the relative indices at any boundary must be interpreted with discretion; for purposes of identification, contrast can be considered chiefly as a preliminary guide.

The emphasis of the present paper is on the distinction of neat and middle phases from each other. There is, of course, the problem of distinguishing either of the phases from other liquid crystalline phases and even at times from certain crystalline textures; there is also the need for distinguishing neat phase in its "isotropic" aspect from truly isotropic liquid phases.

Basically the positive recognition, microscopically or otherwise, of all the many liquid crystalline soap and detergent phases is a large problem of which the present contribution, detailed as it is, is only one part. While much of the present material is applicable to the broader problem, no claim is made that the criteria of Table II by themselves set neat and middle phases apart from all other soap phases. There will, for instance, be cases where a persisting non-geometric texture is encountered in liquid crystalline soap phases other than middle soap, *e.g.*, one of the "waxy" group.

In such cases the phase of the unknown material may be determinable from consideration of composition and temperature, and the relationship to any known adjacent regions, keeping the typical soap phase diagrams in mind. Simple composition changes under the microscope, such as permitting the sample to hydrate or dehydrate partially, are often helpful, as are simple thermal changes. In difficult cases recourse to an x-ray pattern may be necessary to establish the general phase type, particularly to set the waxy phases apart from the simpler smectic structures (50).

Because of the presence of planar areas in the neat phase, the worker in detergents certainly needs to be forewarned that not all apparently isotropic regions are "nigre" or electrolyte solution. Distinguishing a planar neat area from truly isotropic liquid by mechanical or thermal disturbance is described under Texture 122.1. Where the sample cannot be disturbed, convergent or oblique light may be used as discussed under Texture 110.

A further precaution needs to be raised: against the ability of sufficiently viscous nigres to become, and even to remain, anisotropic when flowed. However in such cases the anisotropy will possess no mosaic texture such as is always evident when "isotropic" neat phase areas are disturbed.

It is recognized that the identification scheme of Table II may require some future revisions since it is based on a classification (Table I) which is, to some degree, empirical. For one thing, both phases involved are liquid crystalline and therefore lack such

TABLE II

Selected Microscopic Criteria Used for Recognition of
Neat and Middle Phases

A. NEAT PHASE

I. Planar ("isotropic") areas common, especially 112 and 113.1; form spontaneously or on careful manipulation[a] of cover glass. (Contrast with B-III in middle phase.)

II. Extinction crosses, single (121.2) or in complex combinations (122.1), of negative "optic sign" and broadest at the center; on rotation of stage, crosses pass through "pinwheel" aspect. (In middle phase, positive crosses only; no "pinwheels.")

III. "Mosaic" texture (122.1) formed from planar areas on mechanical[a] or thermal disturbance. Usually rather fine-grained but rarely so much as to prevent characterization by presence of negative extinction crosses and "pinwheels."

IV. Even after mechanical disturbance, never appears less geometric than fine mosaic texture.[b] (Contrast with B-IV in middle phase.)

V. Coarser or better-developed textures not ordinarily formed by digestion.[b] (Contrast with B-V in middle phase.)

VI. Higher birefringence than middle phase.[c]

B. MIDDLE PHASE

I. Fanlike (222.5) or angular (222.6) textures with extinction crosses of positive "optic sign" only; extinction arms remain parallel to crosshairs on rotation of stage, i.e., "pinwheels" absent. (Cf. 122.5 in text.)

II. Non-geometric texture (230). Birefringent but extremely fine-grained with no geometric pattern; may be somewhat striated (232). May persist indefinitely (232.1) or develop (232.2) into geometric texture on standing or warming. (Neat phase is always either planar or geometric; see A-IV.)

III. Does not form planar areas on digestion or careful manipulation. (Contrast with A-I in neat.)

IV. With sufficient mechanical disturbance, geometric textures can be broken down to completely non-geometric texture. (Contrast with A-IV in neat.)

V. Geometric textures develop, if at all, by digestion of non-geometric area (Contrast with A-V in neat) or on formation of middle phase, as by precipitation from isotropic phase.

VI. Lower birefringence than neat.[c]

[a] See discussion of texture 110 in text.
[b] See discussion of texture 122.1 in text.
[c] See discussion in Section II of text.

features as interfacial angles which can be used to distinguish definitely between fully crystalline materials. Furthermore both phases are either of the same structural type, smectic, or of two closely related types from Hermann's classification (see Section III following). In addition, the variety of textures exhibited by each phase, and the at least partial dependence of texture on conditions of formation, warns of the possible existence of textures not yet encountered.

Nevertheless it is felt that the scope of compositions and conditions on which the classification is based indicates its value as a practical device for phase studies of soaps and synthetic detergents, even if some minor revisions prove necessary. The classification furthermore serves as a necessary step towards a fuller acquaintance with the multiplicity of liquid crystalline soap and synthetic detergent phases, some very little studied and others very likely not even encountered as yet.

III. *Structural Considerations.* With the exception of the non-geometric textures (230) in the middle phase, all the textures summarized for neat and middle phases in Table I either are specifically associated with the smectic state by Friedel (13) or are possible variations of Friedel's textures. To this extent previous statements that both phases are smectic (7, 23, 40, 45, 54) are substantiated.

Certain of the present observations however suggest that there may be a fundamental structural distinction between these two phases, presumably along the lines formulated by C. Hermann (20).

The principal existing evidence in favor of such a structural distinction is the inability of middle phase to reorient spontaneously into a planar arrangement corresponding to the 110 textures so easily and commonly assumed by neat soap. This difference in behavior might be passed off simply as a result of the

large difference in fluidity if it were not for the following circumstance. In the hydration of certain soaps there occurs a phase or other condition (see below) which exhibits a consistency like that of middle phase yet which does orient spontaneously (Figures 25-6), and in time completely, into a planar arrangement. This behavior lends weight to the point of view that the absence of such orienting tendency in the middle phase reflects a structural difference between it and neat.

The absence, in the middle phase, of any focal conic geometry simpler than the fanlike texture may also have a structural origin.

However, while very useful as a somewhat empirical method of phase identification, microscopic texture by itself is not so far a sufficient basis for establishing a fundamental structural difference between the neat and middle phases. The final answer must be based on studies by several different techniques, certainly including x-ray diffraction.

The above self-orienting, though highly viscous, condition has been provisionally designated "viscous neat phase" for two reasons. a) On either warming or drying, it passes into neat phase of conventional fluidity. b) It exhibits textures (the planar regions as well as "oily streaks" described below) analogous to those of the neat phase rather than the middle. While "viscous neat" is suspected of being a separate phase, it could conceivably be a high-moisture, low-temperature, high-viscosity corner of the neat region. "Viscous neat" is observed, for example, at room temperature in potash soybean-oil soap of low electrolyte content and at about 40% water. Pressure on oriented isotropic areas of "viscous neat" yields, not the fine, focal conic, "mosaic" texture of ordinary neat phase, but an angular mosaic (Figure 27), suggesting a closer approach to crystallinity. On cooling the above soybean soap composition from the true neat state, conversion to "viscous neat" is evident as a replacement of the fine, focal conic cross-banding and rounded contours of the oily streaks (Figure 28) by an angular, jointed texture (Figure 29) consisting of a small number of areas of uniform extinction. In spite of this approach to crystalline character, the jointed "oily streaks" slowly but spontaneously disappear leaving a planar area.

The facetted droplets (1) and angular myelinic figures (21), mentioned in the literature, are presumably related to the above "viscous neat" textures.

Experimental Methods

The techniques involved are relatively simple. Merely pressing out the sample between slide and cover glass permits examination for many minutes without water loss even in fairly warm systems, except at the edges of the preparation. This simple technique permits examination of a more extensive field than in a flat capillary, allows a choice of sample thickness, and expedites necessary manipulation of the sample by pressing or sliding the cover glass. Simple moisture control, even over periods of several days or more, can be added by ringing the under edge of the coverglass with a medium, such as Aroclor No. 1262 (Monsanto), which is free of volatile solvent. Better moisture control up to 80-90°C. with retention of the foregoing advantages is attained by a simple screw-clamp arrangement which closes off the edge of the cover glass with a thin rubber gasket. The efficiency of such moisture control was evident from the fact that certain middle soaps, which went to neat soap promptly at the edges of an unprotected preparation, formed no neat with the Aroclor or gasket seal. Where a glass seal is required, flattened capillaries similar to those described by Doscher and Vold (8) are employed and found satisfactory to some 300°C. or more, if sufficiently thick-walled.

Where only approximate control of temperature is required and manipulation of the sample is desired, the unsealed or gasket-sealed preparations are employed and warmed with an electric hot-wire, arranged preferably below a raised slide; in much of the present work this procedure was adequate since from previous phase studies the phases under examination were known to have a wide temperature range of existence. Where more precise temperature control is required, the flattened capillaries are heated in a precision micro-oven designed by Dr.

Quimby of this laboratory and equipped with a thermocouple.

Since the texture of neat and middle phases depends partly on sample thickness, it has become a frequent practice here to make a wedge-shaped preparation by resting one side of the cover glass on another cover glass or a fragment. In this way more than one texture may be studied in one preparation and the most satisfactory thickness for each selected. As a rule, the most definite textures are obtained in layers that are not too thick; a good rule is to rely on areas which exhibit intermediate-first-order interference colors: light grays and yellows. Exceptions exist, of course, but thinner layers may appear too dim or the texture too diffuse, and thicker layers may be confused by the effects of other layers than the one in focus. Ordinarily a 16-mm. objective is preferable, but for fine textures an 8-mm. or even a 4-mm. may be used profitably.

The saturated single soaps were made by neutralizing fatty acid to phenolphthalein in boiling 95% alcohol with saturated aqueous NaOH or KOH, driving off the alcohol in a steam oven, and finally drying to constant weight at 150°C. The oleate was prepared similarly but dried at 100°C. in a closed system swept with anhydrous nitrogen. The commercial soaps were prepared on a laboratory scale by conventional soap "boiling."

Hydration of the saturated soaps was carried out by sealing soap and water into glass tubes under water-pump vacuum, and holding 3-4 hours at 100°C.; neat soap compositions could be homogenized by frequent vigorous shaking, but middle soap tubes were cooled once, the contents mixed with a spatula and resealed for further heating. For the oleates the elevated temperature was only 70°C. The final moisture content was determined from loss in weight after one hour at 150°C. for all soaps but the oleates, which were dried to constant weight at 70°C. in a vacuum oven.

Summary

The mesomorphic or "liquid crystalline" neat and middle phases encountered in aqueous systems of soaps and synthetic detergents differ considerably in plasticity. Nevertheless, in fundamental phase studies or the examination of commercial products and processes, identification of these two phases has hitherto been uncertain, particularly when they are mixed with each other or with other phases; even under the polarizing microscope, their identification has not been positive since, by the classical criteria for identifying mesomorphic phases, both are "smectic."

The present work reveals additional criteria by which the two phases may be satisfactorily distinguished. In the first place, there are non-geometric textures exhibited by middle but not by neat. Conversely, there are planar textures exhibited by neat but not by middle. Furthermore there are important systematic differences even among the focal conic textures upon which the smectic nature of the two phases has previously been predicated.

While the microscopic method now makes possible the identification of phase mixtures, it serves also as a rapid method even where one-phase compositions are concerned.

This study is primarily descriptive in its present state of development, but the existence of systematic microscopic differences between these two nominally smectic phases, coupled with their well-known and pronounced difference in consistency, suggests a fundamental structural distinction between them.

Much of the present subject-matter applies also to such materials as certain wetting agents and dyes, as well as phosphatides and certain other biological substances.

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CORRECTION

T. P. Hilditch reports that in his Letter to the Editor, appearing in the October 1954 issue of the Journal of the American Oil Chemists' Society, page 433, there were two errors. Lines 11-12 in column 2 should read: "the GS_2U glycerides form a smooth curve." Lines 21-22 should read "but monosaturated glycerides never more than 45-50%."

ABSTRACTS . . . . R. A. Reiners, Editor

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• Oils and Fats

Ralph W. Planck, Abstractor
Dorothy M. Rathmann, Abstractor
Sin'itiro Kawamura, Abstractor

Chemical composition of cerebral arteries. The concentration of lipids and minerals compared with those in the internal carotid. R. C. Buck, J. C. Paterson, and R. J. Rossiter(Dept. Biochem., Univ. Western Ontario, London, Ontario). *Can. J. Biochem. and Physiology* 32, 539(1954). The concentration of total cholesterol, total phospholipid, nonlipid phosphorus, calcium, and fat-free dry residue was determined in the internal carotid and cerebral arteries obtained at autopsy from a series of 14 male subjects ranging in age from 40 to 85 yr. By the method of rank correlation it was found that for both vessels the concentration of total, free, and ester cholesterol was significantly correlated with both age and severity of the atherosclerosis. Ester cholesterol expressed as a percentage of total cholesterol was also significantly correlated with age and the severity of the disease process.

Doedorizing vegetable oils. Anon. *Chem. Eng.* 61(10), 256 (1954). A discussion of U. S. Patent 2,674,609 is given. In this process oil is deodorized at 20-60 microns pressure and 190°-250°F. for 10-48 minutes.

X-ray diffraction and electron microscope studies on the brain lipide strandin. J. B. Finean(Dept. Biology, Mass. Inst. Tech., Cambridge, Mass.). *Arch. Biochem, Biophys.* 52, 38(1954). The electron micrographs of thin layers of strandin show a fairly regular rectangular arrangement of particles measuring approximately 60 x 100 x 100 A., the smallest dimension corresponding to the thickness of the layers. X-ray diagrams of thick crystalline plates show intense low-angle diffractions in three mutually perpendicular directions which correspond roughly to these dimensions. The diffraction spacings of different strandin preparations vary somewhat, and the effects of alcohol, and more particularly of water, suggest that strandin may be a complex or series of complexes in which some of the association of components is more physical than chemical.

A system of characterization of common organic acids. R. T. Wendland and D. H. Wheeler(North Dakota State College, Fargo, N. D.). *Anal. Chem.* 26, 1469(1954). Organic acids containing carbon, hydrogen, and oxygen only can be divided into four well-defined classes based on common physical properties and simple chemical tests. Identification of the drying oil acids calls for ultraviolet absorption studies, or chemical processes of bromination, hydroxylation, and isomerization. Practical significance of the work lies in the increased ease of identification of a large number of compounds encountered frequently in research and industrial operations.

Product control at Colgate-Palmolive Ltd. *Canadian Chemical Processing,* 38, No. 10, 96(1954). A description is given of the new $1,500,000 control laboratory at Colgate-Palmolive in Canada.

Vegetable oils. III. Mallotus philippinensis Muell. Arg. seed oil. R. C. Calderwood and F. D. Gunstone(The University, Glasgow). *J. Sci. Food Agr.* 5, 382-7(1954). Characteristics of kamala-seed (*Mallotus philippinensis* Muell. Agr.) oil are tab-

ulated and compared with previously reported values. Low temperature fractional crystallization, spectrophotometric examination before and after alkali-isomerization, hydrogenation, acetylation, methylation, and fractional distillation yielded data which show that the mixed acids of kamala-seed oil consist of palmitic 18, oleic 28, linoleic 18, and kamlolenic acid 36%. Because the oil polymerizes when heated with acetic anhydride, acetyl values were determined on the mixed hydrogenated esters. The isolation of a-kamlolenic acid and isomerization to β-kamlolenic acid by ultraviolet irradiation of a benzene solution containing iodine are described. a-Kamlolenic acid had m.p. 72°-5°C., and absorption maxima at 262, 271 and 282 mμ. β-Kamlolenic acid had m.p. 85°-7°C. and absorption maxima at 259, 269 and 280 mμ. Repeated recrystallization of β-kamlolenic acid lowered the $E_{1cm.}^{1\%}$, presumably by oxidation. Ozonolysis of methyl a-kamlolenate yielded methyl 8-formyloctanoate, confirming previous reports that a-kamlolenic acid is an 18-hydroxyoctadeca-9:11:13-trienoic acid. During the isomerization of a- to β-kamlolenic acid, one or more *cis* bonds change to *trans* bonds. The relationship of kamala-seed oil to other oils from plants of the Euphorbiacae family, and the possibilities of using kamala-seed oil as a drying oil are discussed briefly.

Soybeans and products futures markets. J. S. Schonberg(Uhlmann Grain Co., Chicago, Ill.). *Soybean Digest* 14(11), 48-51 (1954). Futures contract markets for soybeans, oil and meal are discussed.

Loss of fat during souring of cream. J. E. Roe and H. Edelson (Food and Drug Admin., Dept. of Health, Education and Welfare, Kansas City 6, Mo.) and W. E. Polzen. *J. Assoc. Off. Agr. Chemists* 37, 849-56(1954). Analyses of 24 samples of coffee cream (18% fat) and 26 samples of whipping cream (30% fat) during souring at room temperature showed that loss of fat is not measurable by the Babcock method over a 4-day storage period. Losses are detectable by the Roese-Gottlieb method, but over a 7-day period amount to only about 0.1% of the total per cent of fat per day.

Report on ether extract in fish. H. M. Risley(Food and Drug Admin., Dept. of Health, Education and Welfare, Seattle 4, Wash.). *J. Assoc. Off. Agr. Chemists* 37, 605-7(1954). Results of a committee test of a suggested rapid method for the determination of fat in canned salmon are summarized. A modification in the drying method and extension of the work to other species of fresh, frozen and canned fish are recommended.

Surplus butter disposal and soybean oil. S. Riepma(National Assoc. Margarine Manufacturers). *Soybean Digest* 14(11), 72, 74, 76(1954). Possible methods of disposing of Commodity Credit Corporation-held surpluses of fats and fat products are discussed in terms of effects on normal food fat markets.

World fat and oil supplies. P. E. Quintus(Fats and Oils Div., Foreign Agricultural Service). *Soybean Digest* 14(11), 46-7 (1954). World production and distribution of fats and oils are reviewed. Although per capita supplies are now probably ahead of the prewar levels, total supplies do not appear excessive. Distribution problems create local imbalances. U. S. has substantial reserves for export.

Report on eggs and egg products. F. J. McNall(Food and Drug Admin., Dept. of Health, Education and Welfare, Cincinnati 2, Ohio). *J. Assoc. Off. Agr. Chemists* 37, 818(1954). Several