Characterization of Alkali Soaps by Electron Microscopy

By Gopal S. Hattiangdi[1] and Max Swerdlow

The morphological differences between several closely related alkali soaps have been determined by the techniques of electron microscopy. The crystalline alkali soaps consist of an interlocked mesh of bundled fibers, whereas the liquid-crystalline soaps exhibit a flagellar and/or featureless phase. The micellar groupings for the individual soaps are unique, and a scheme based upon the electron micrographs is suggested for their characterization. The structures of lithium, sodium, and potassium palmitates are closely related. The laurate, palmitate, and stearate of sodium also exhibit homologous structures.

The results of these morphological investigations offer a rapid and accurate means of identification and have been successfully applied to the problem of characterizing commercial soaps of unknown composition.

I. Introduction

When alkali soaps are heated, desiccated, hydrated, or ground mechanically, they pass through a remarkable series of forms, each constituting a definite stable phase existing over a definite range of temperature and/or composition. Attempts have been made to characterize these phases by means of X-ray diffraction patterns, but the data reported in the literature are rather anomalous. Buerger, Smith, Ryer, and Spike [1] [2] believe that sodium soaps exist in seven distinct crystalline phases (κ, ζ, μ, ϵ, δ, α, and η); in addition, they suggest several others (α', α'', η', η'', etc.), which are closely related to these seven. Ferguson, Rosevear, and Stillman [3] report only four solid soap phases (α, β, δ, and ω), their omega phase corresponding to Buerger's kappa and eta phases and their beta, to Buerger's epsilon and zeta phases. Also, Ferguson's omega phase is believed [3] to be identical to the gamma phase reported several years earlier by deBretteville and McBain [2]. Added to this rather confusing use of different designations for the same

phase is the large amount of somewhat conflicting data reported by these investigators, a general idea of which is presented elsewhere [4].

The electron microscope, with its high resolving power, has been used with considerable success in recent years to study a variety of colloidal systems. The curd fibers of sodium laurate have been investigated by Marton, McBain, and Vold [5] with the aid of an electron microscope, and have been shown to consist of a mass of fibers that are thin ribbons whose widths are reported to be integral multiples of approximately twice the length of the soap molecule.

The present investigation is of an exploratory nature. It is designed to reveal morphological differences between eight pure alkali soaps representing different homologous cations and anions, and to characterize some commercial soaps of unknown composition.

II. Materials Used

The soaps investigated were the palmitates of lithium, sodium, potassium, rubidium, and cesium, and sodium laurate, sodium stearate, and sodium oleate. All the palmitates were prepared by neutralizing a solution of palmitic acid in

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[2] Figures in brackets indicate the literature references at the end of this paper.

95-percent ethyl alcohol with an alcoholic solution of the corresponding alkali hydroxide and drying the product to constant weight at 105° C. The sodium soaps were prepared by neutralizing a solution of the fatty acid in 95-percent ethyl alcohol with sodium ethylate; sodium laurate and sodium stearate were dried to constant weight at 105° C, and sodium oleate was dried under reduced pressure at 40° C. The constants of the fatty acids used are given in the following tabulation:

Acid	Equivalent weight	Iodine number	Melting point
			° C
Lauric (Eastman Kodak Company's best quality)	202. 6	0. 05	45. 0
Palmitic (Eastman Kodak Company's best quality)	257. 0	. 0	62. 2
Stearic (Kahlbaum, Schering's pure quality)	284. 3	. 0	69. 0
Oleic (British Drug Houses' pure quality)	288. 3	85. 8	-----

Two toilet soaps (T3 and T8), one manufactured in the United States and the other in India, and samples of washing (W5) and shaving (S5) soaps (both manufactured in India) were the same as those used for the X-ray diffraction studies [4]. They were obtained from the retail market and were examined without any purification. Chemical analysis disclosed that the cation was sodium in all of the four soaps.

III. Experimental Procedure

The soaps were dispersed in anhydrous n-butyl alcohol by milling with a mullite mortar and pestle for 5 minutes in an air conditioned room at 24°C and 60-percent relative humidity. The suspension was cast on Formvar (polyvinyl formal) plastic films supported by 200-mesh stainless steel specimen screens. Upon drying, the specimens consist primarily of the undissolved soaps, since their solubility in n-butyl alcohol is very low.

Since metallic shadowing adds contrast as well as a three-dimensional aspect to the surface details, a very thin coating of evaporated chromium was deposited obliquely (at an angle whose tangent equals 5 cm/20 cm) upon the soap specimens. This was achieved in a manner similar to that of Williams and Wyckoff [8] by slowly evaporating 100 mg of pure (electrolytically deposited) chromium metal with a current of 30 amp at 15 v in about 10 min at a pressure of 10^{-5} mm of Hg. The chromium was outgassed for about 20 min with 10 to 20 amp of current through the tungsten-wire basket. During the deposition of the metal, elevations and depressions on the surface of the soap specimen cast shadows characteristic of its contour; where no metal is condensed, transmission of the incident beam is maximum, and where thick elevations occur, electron scattering is maximum and little or no electrons are transmitted. More details concerning the technique of metallic shadowing used here are reported elsewhere [7].

The shadowed specimens of the soaps were examined and photographed with an RCA—EMU (50 kv) electron microscope. The sampling plan included at least eight separate specimens for each soap. Representative micrographs of characteristic areas for the individual soaps are presented in figures 2 to 13, the linear magnification in each case being denoted below each reproduction. Negative prints are shown in the figures. For proper interpretation of the surface features and structures, they may be viewed as though the soap formations were obliquely illuminated.

IV. Results and Discussion

One of the most characteristic features of the soaps when viewed through the electron microscope is that many of them exhibit an interlocked mesh of fiber bundles of varying diameters and different degrees of twist but with a general tendency toward retaining both a criss-cross and a parallel structure (fig. 7, A). The diameters of the fibers are dependent not only upon the nature of the soap but also upon the concentration and rate of crystallization, inasmuch as denser areas of the same soap specimen exhibit stouter fibers than those found in regions of lower concentration. Although any measurement and subsequent interpretation of the ultimate fiber widths in terms of absolute units seems questionable, a qualitative comparison of dimensions and structures between soaps is reasonable. The growth of the fibers in parallel rows at right angles to each branch, either in the same or in different planes, is interesting and is probably related to

the monoclinic angle (the angle of tilt of the hydrocarbon chains, β). When $\beta = 90°$, preferred orientation of the lateral branches is a maximum. The packing of the hydrocarbon parts of the soap molecules can be achieved in several ways. One possible manner, constructed from known values for the bond distances, bond angles, and atomic radii [6], is shown in figure 1, in which the packing of the soap molecules in the fiber is restricted to a lateral association of the hydrocarbon chains.

Another outstanding fact revealed by the electron microscope is that each soap exhibits unique and distinct features, such as a curdy mass, an octopean mass, filamentous, hairy, frond-like, and sheaf-like formations. The presence of these formations as well as the increase or decrease in their degree of crystallinity, internal and external structure, etc., are dependent upon the position of the soap in the cationic or anionic series. That these formations are characteristic and reproducible is shown consistently by the presence of approximately the same number, size, and shape of such formations in different specimens of the same soap prepared under identical conditions. These are probably due to a type of structural unit, such as a micellar grouping, within the soap fibers and are probably related either to the mosaic structure of the surface of crystals or to the crystal of the individual phases. Before any correlation of statistical significance can be made with regard to external morphology and molecular arrangements, further studies are necessary. Whatever the interpretation, these patterns serve as excellent guides for a quick characterization of the alkali soaps notwithstanding possible artifacts.

1. The Alkali Palmitates

Lithium palmitate is characterized by thick curdy clumps. Whether present singly or joined together with one or more of such clumps, they always exhibit a tendency for the curd to grow out in a frond-like formation that is usually opaque to the electron beam and lacks fine structure (fig. 2,A,B, and C). The primary pattern for sodium palmitate is revealed in the less dense areas as a very fine network of interlaced fibers that show a perceptible periodic structure (fig. 3,C). On this background are developed mounds similar to those for lithium palmitate but with fine spicular fibers fanning out from them (fig. 3,B). In the less concentrated regions, these mounds have the con-

figuration of the fan palm (fig. 3,A). The resemblance of the sheaf-like appearance found in figures 2,C and 3,A is noteworthy. Potassium palmitate, like sodium palmitate, appears basically crystalline (fig. 4,B and C), and the fibers show a spiral periodicity that is not exhibited by lithium palmitate. Furthermore, the fibers tend to pack laterally with their periodic structure in register (fig. 4,B). In addition to this highly crystalline state, this soap exhibits a featureless liquid-like phase (fig. 4,A). In contrast to the somewhat analogous behavior of lithium, sodium, and potassium palmitates, rubidium and cesium palmitates show almost entirely different habits. Rubidium palmitate is characterized by a liquid-like phase from which small spheroidal particles seem to separate (fig. 5,B), the larger aggregates being present as terraced mounds of irregular shape (fig. 5,A and C). Cesium palmitate also exhibits a liquid-like phase that is present in the form of amorphous ribbon-like films (fig. 6,A). Figure 6,B and C show thin long fibers, which probably have a greater degree of crystallinity, developing from an agglomerated mass of this liquid phase.

In summation, it might be said that of the five homologous alkali palmitates, lithium, sodium, and potassium exhibit a somewhat similar appearance, whereas rubidium and cesium are distinctly different. The first three soaps are differentiated by the mounds of curd-like material from which fibers grow. The degree of crystallinity, orientation, and periodicity of these fibers are least for lithium palmitate and most for potassium palmitate. Rubidium and cesium palmitates have a predominant liquid-like phase unlike the other three soaps, which exhibit a linear network of interlaced fibers. Rubidium palmitate is characterized by very small terraced mounds of eccentric shapes, whereas cesium palmitate exhibits agglomerated masses, from which thin long fibers grow out in all directions.

2. The Sodium Soaps

Sodium laurate has a basic structure of curd-like fibers intermeshed in a more or less regular parallel formation (fig. 7,A). The resemblance between the unshadowed specimen (fig. 7,B) and that published by Marton, McBain, and Vold [5] is very interesting because the soap structures seem to be independent of the two different methods of

specimen preparation and of the ionic or monionic nature of the solvents used. In the less concentrated areas, the bundled fibers appear to be flattened out into a sheaf-like pattern (fig. 7,C). There also appears a thorny protrusion in these fibers. Sodium palmitate exhibits finer fibers, and sodium stearate has the finest (fig. 8,A), but both these soaps have a parallel bundling similar to that for the laurate. Sodium stearate has extremely fine fibers developed in dendritic forms (fig. 8,C). By contrast, the basic structure for sodium oleate consists of a very stout fibrous network, the less concentrated areas showing a fine swirled flagellar formation (fig. 9,A). From this predominant phase large micellar groupings develop with an octopean structure—a semicrystalline mound in the center and curling fiber bundles of varying diameters emanating in all directions (fig. 9,B).

In summation, it might be said that the sodium soaps of the saturated fatty acids exhibit a homologous behavior, characterized by a meshwork of interwoven fibers laid out in a regular linear formation and a sheaf-like bundling of the finer fibers (fig. 8,B, 3,A, and 7,C). The fineness of the sheaf-like formations varies for the sodium soaps in the order: laurate < palmitate < stearate. Sodium oleate exhibits a very different behavior, characterized by a lack of linearity and is probably due to the essentially liquid-crystalline nature of this soap.

The increase in the periodic spacings of the soap fibers with increasing molecular weight of the soap (LiP<NaP<KP and NaL<NaP<NaStr) suggests their possible correlation. This is brought out in the tabulation below, in which data are presented for the periodicity for the alkali soap fibers as found in the original electron micrographs.

Soap	Molecular weight	Approximate periodicity
		A
Sodium palmitate_____	278. 3	500
Potassium palmitate_____	294. 4	675
Sodium stearate_____	306. 3	750

The periodic structure that results from a type of stress imposed upon the growth of the soap fibers is exhibited by those soaps that are crystalline in nature and are salts of the saturated fatty acids. Other factors that have an important bearing on the amorphous and/or crystalline nature of the soaps are the degree of hydration, composition, temperature, pressure, extent of mechanical treatment, and rate of precipitation. Assuming that all these factors are similar for the various soaps, it seems reasonable to conclude that for the soaps with the same *anion*, the strain is probably caused by the heavy cation attached to the fatty acid radical; and for the soaps with the same *cation*, the strain is brought about by the inertia of the heavy hydrocarbon chains (fig. 1).

3. Application to Commercial Soaps

Electron micrographs of the samples of two toilet soaps exhibit a network of fine interlaced fibers (figs. 10, B and 11, C); numerous mounds of curd-like material from which fine fibers showing traces of periodic structure grow out (figs. 10, A and 11, A); and a swirled flagellar formation (figs. 10, C and 11, B). The first two characteristics are typical of sodium palmitate and the third of sodium oleate. Toilet soaps are usually made from oils of high palmitate-oleate content. Analysis by X–ray diffraction cannot definitely identify the components of the binary system, since only an average value for the two long spacings and overlapping peaks for the short spacings are obtained [4]. On the other hand, observations by electron microscopy are in excellent agreement with chemical analysis, and in such cases prove to be not only more rapid but more accurate than X-ray diffraction or other methods of analysis.

The washing (laundry) soap (fig. 12) is characterized by an essentially liquid-like phase from which aggregates of indefinite shape and little fine structure separate. The extremely primitive state of these aggregates and the absence of any appreciable number of fiber or flagellar formations makes identification of this soap uncertain, although the possible existence of sodium palmitate is indicated. X-ray diffraction data [4] show that the long-spacing value for this soap does not correspond to that for any single pure sodium soap.

The shaving soap consists of a very fine network of interlaced fibers, which show a periodicity of about 600 A (fig. 13, C), and curd-like mounds from which fine short fibers emanate (fig. 13, A and B). The first may be expected from a mixture of sodium palmitate and sodium stearate, and

the second from sodium palmitate alone. X-ray diffraction data [4], however, indicate the presence of several phases of sodium plamitate and do not reveal the presence of any other type of soap.

V. References

[1] M. J. Buerger, L. B. Smith, F. V. Ryer, and J. E. Spike, Jr., The crystalline phases of soap, Proc. Nat. Acad. Sci. **31**, 226 (1945).

[2] A. deBretteville, Jr. and J. W. McBain, X-ray evidence for a third polymorphic form of sodium stearate, Science **96**, 470 (1942); X-ray diffraction investigation of sodium stearate from room temperature to the melting point, J. Chem. Phys. **11**, 426 (1943).

[3] R. H. Ferguson, F. B. Rosevear, and R. C. Stillman, Solid soap phases, Ind. Eng. Chem. **35**, 1005 (1943).

[4] G. S. Hattiangdi, Characterization of some commercial soaps by X-ray diffraction, J. Research NBS **42**, (1949) RP1972; G. S. Hattiangdi, W. W. Walton, and J. I. Hoffman, Some physical-chemical properties of aqueous solutions of soaps and soapless deturgents, J. Research NBS **42** (1949) RP1974.

[5] L. Marton, J. W. McBain, and R. D. Vold, An electron microscope study of curd fibers of sodium laurate, J. Am. Chem. Soc. **63**, 1990 (1941).

[6] L. Pauling, The nature of the chemical bond (Cornell University Press, Ithaca, N. Y., 1940).

[7] M. Swerdlow and G. S. Seeman, A method for the electron microscopy of wool, J. Research NBS **41**, 231 (1948) RP1921; Textile Res. J. **18**, 536 (1948).

[8] R. C. Williams and R. W. G. Wyckoff, Applications of metallic shadow-casting to microscopy, J. Applied Phys. **17**, 23) (1946).
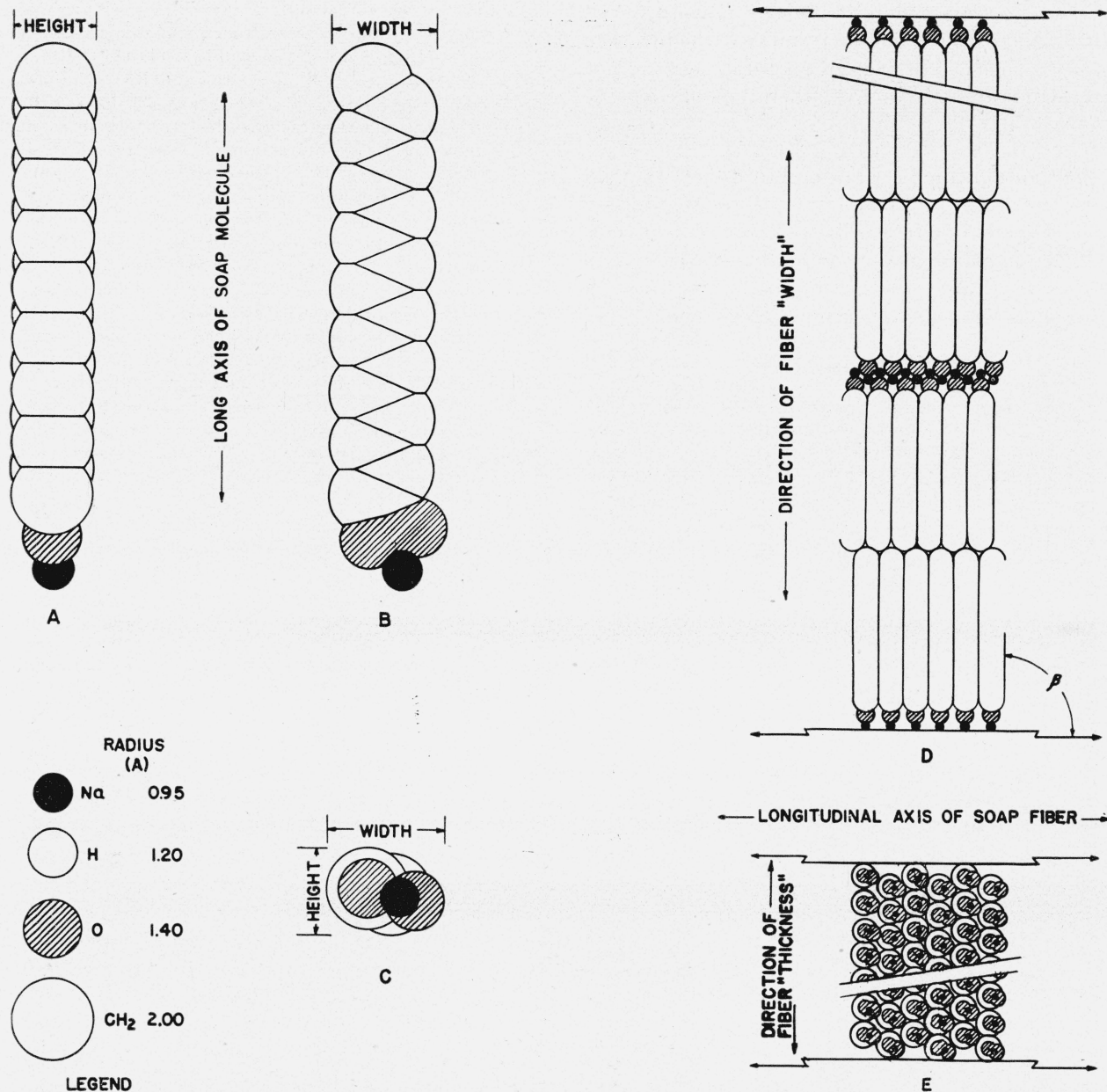
FIGURE 1. *Schematic representation of molecular packing*

This shows the soap (sodium stearate) molecule as viewed from different directions. Views D and E are drawn to approximately one-third the scale indicated for views A, B, and C. A, viewed in a direction perpendicular to the long axis of the molecule but lying in the plane of the hydrocarbon chain; B, perpendicular to both the long axis of the molecule and the plane of the carbon atoms in the chain; C, parallel to the long axis of the molecule as viewed from the carboxylate end; D, sodium stearate molecules (probably 10 or more in number) packed laterally end to end to form a linear chain, thus contributing to the "width" of the fiber. The orientation is not necessarily perpendicular as shown, but tilted at an angle, β, which varies from soap to soap; E, the packing of molecules viewed along a direction parallel to both the long axis of the molecules and the plane of the carbon atoms in the chain (corresponding to view C). Such a packing in the plane of the carbon atoms takes place almost indefinitely and contributes to the "length" of the fiber. The "height", or "thickness", of the fibers is dependent upon the number of soap molecules packed in a direction perpendicular to the plane of the carbon atoms but parallel to the long axis of the soap molecules.
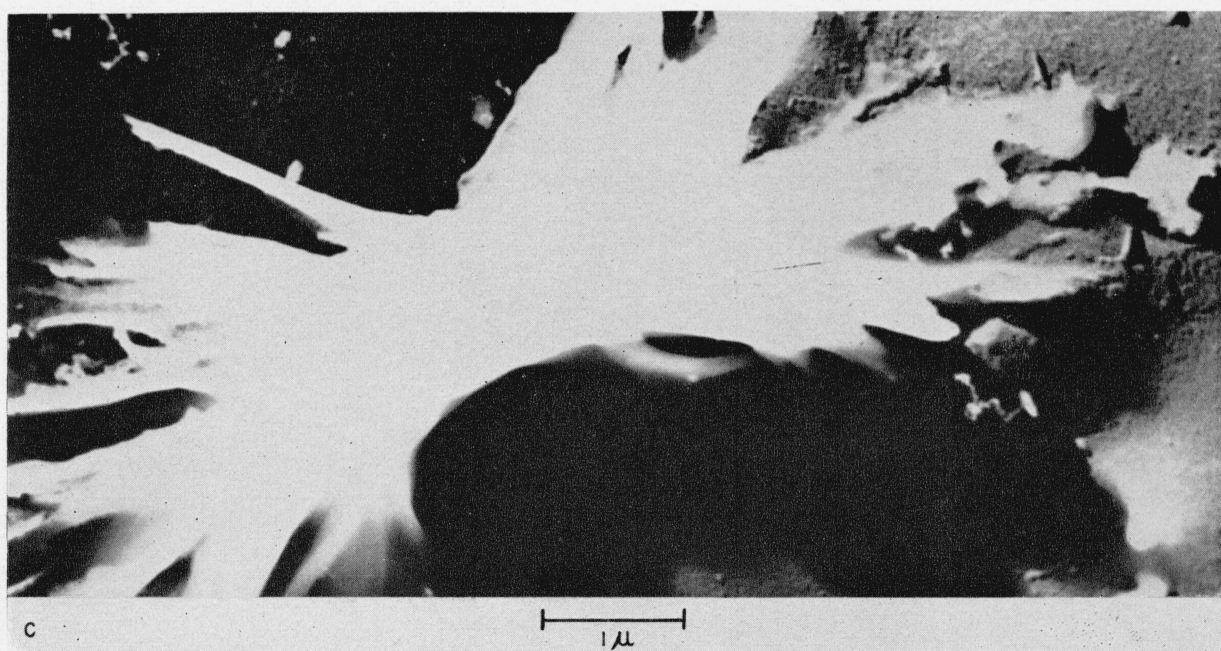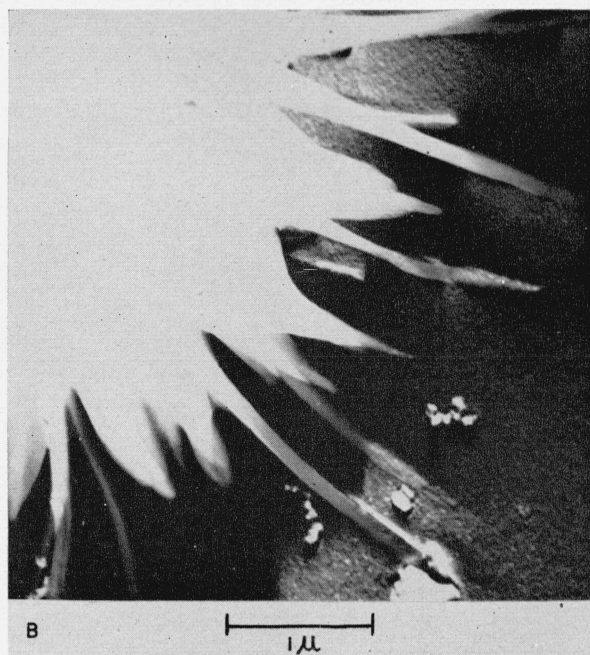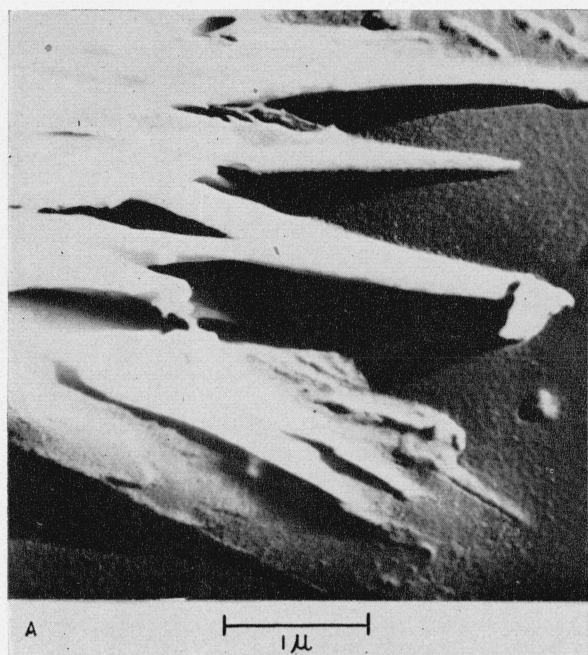
FIGURE 2. *Lithium palmitate*

	Total magnification	Electronic	Optical
A	19,000	9,500	2.0
B	19,000	9,500	2.0
C	18,700	5,200	3.6

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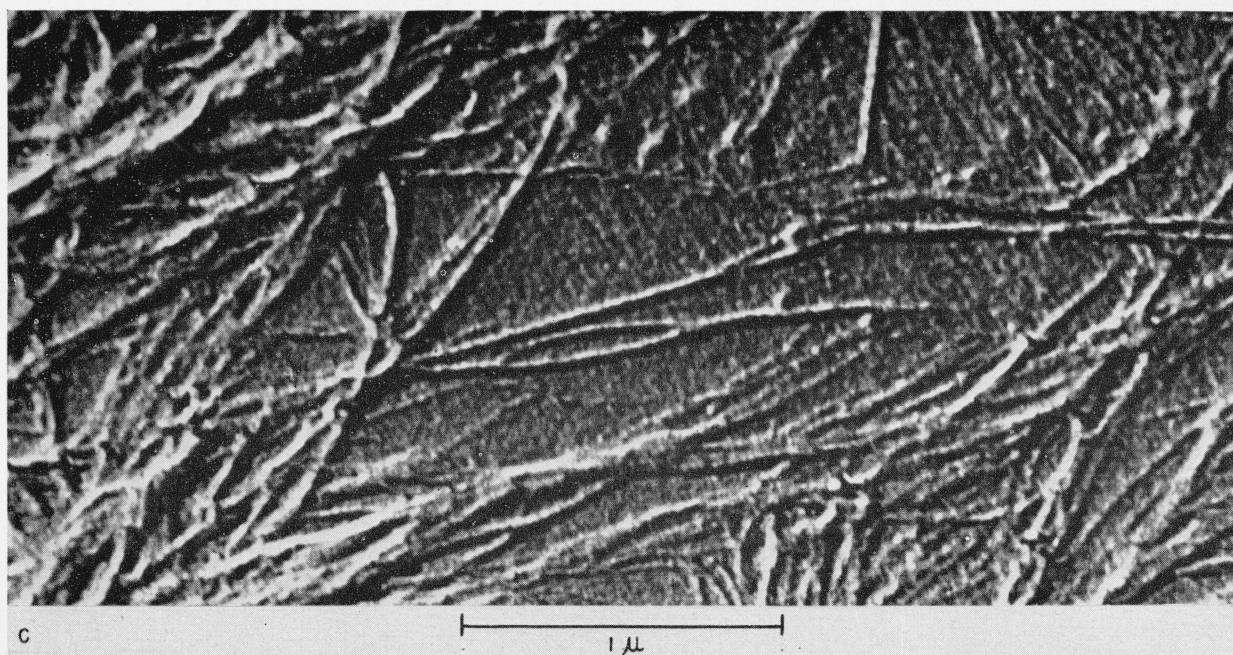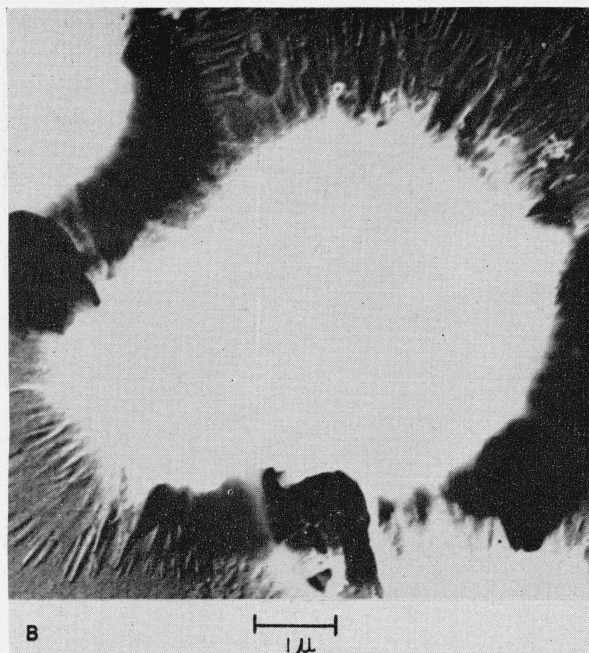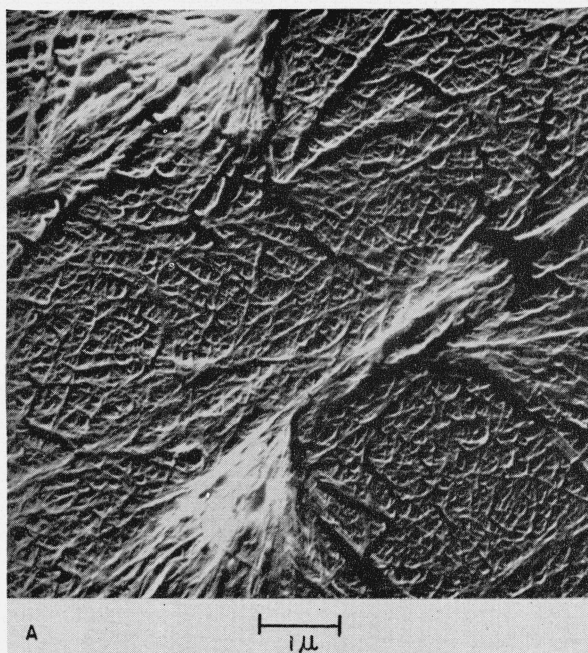
FIGURE 3. *Sodium palmitate*

	Total magnification	Electronic	Optical
A	10,400	5,200	2.0
B	10,400	5,200	2.0
C	42,800	9,500	4.5
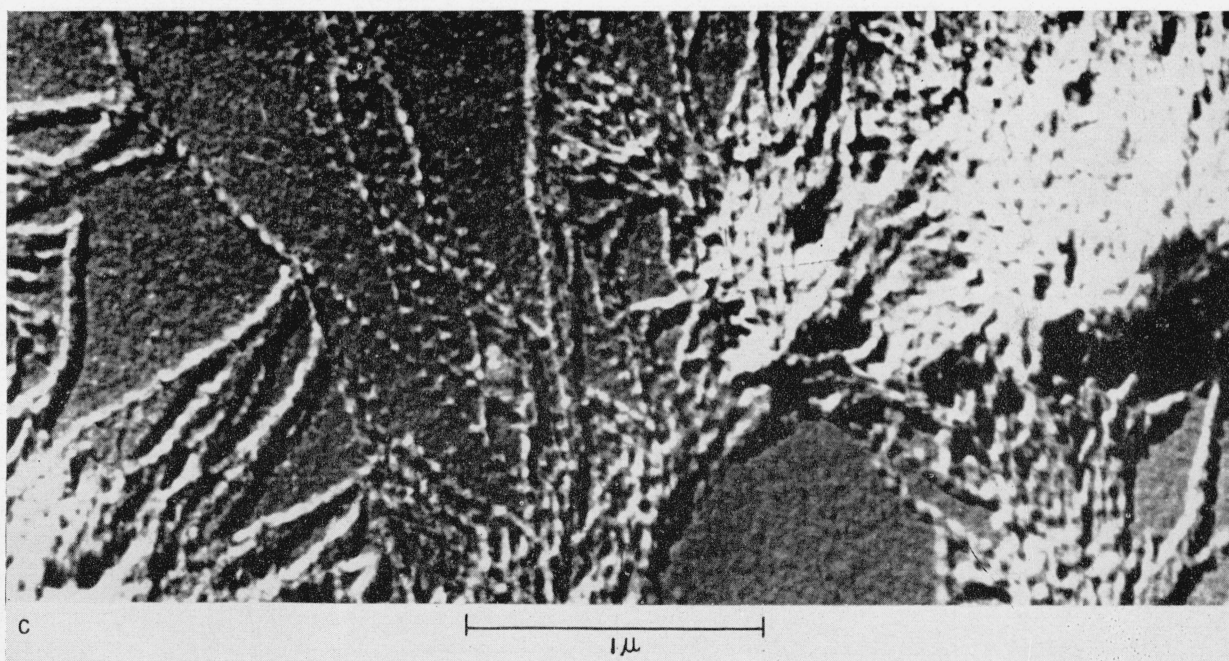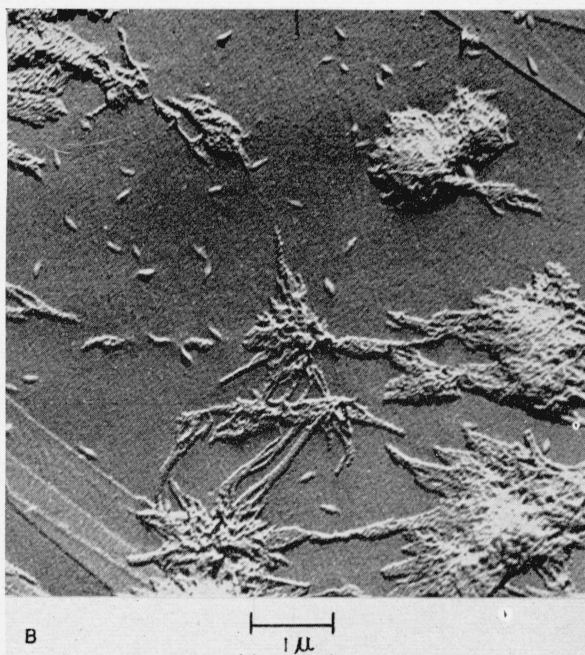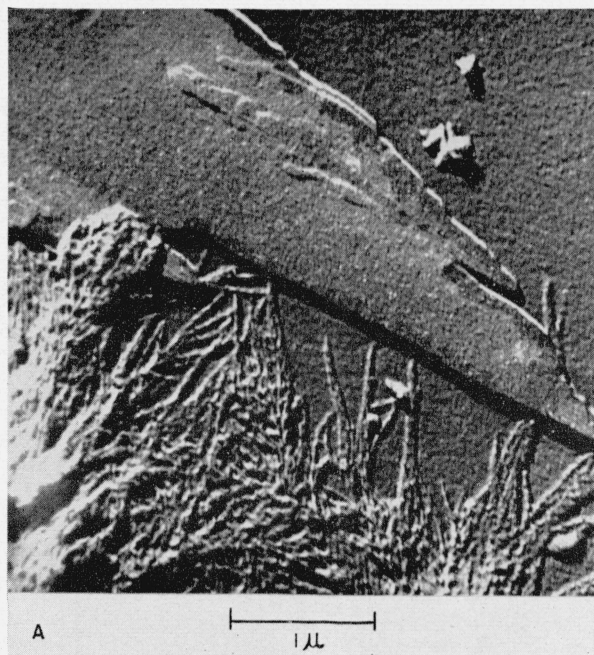
FIGURE 4. *Potassium palmitate*

	Total magnification	Electronic	Optical
A	19,000	9,500	2.0
B	10,400	5,200	2.0
C	39,900	9,500	4.2
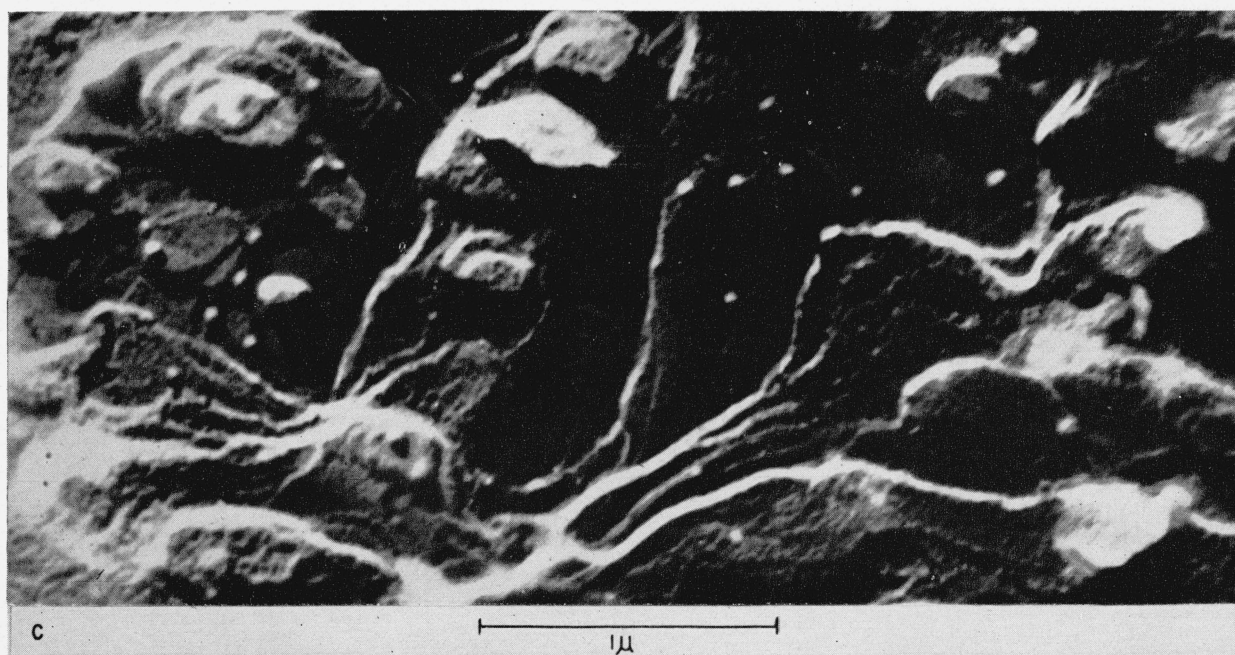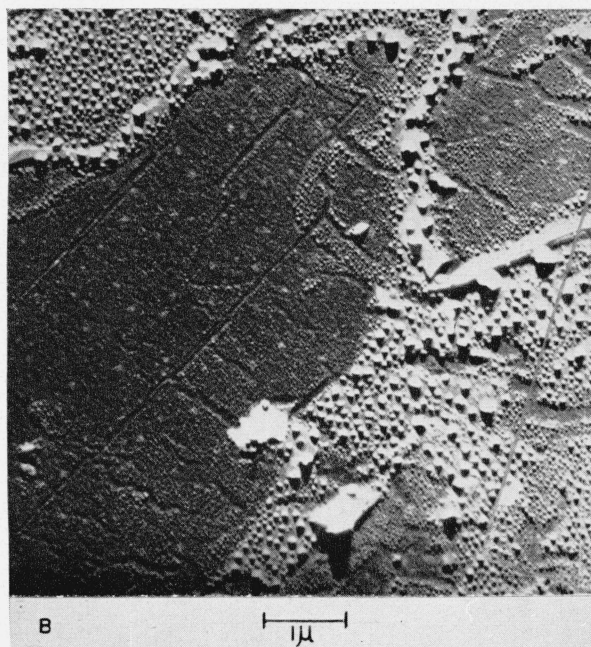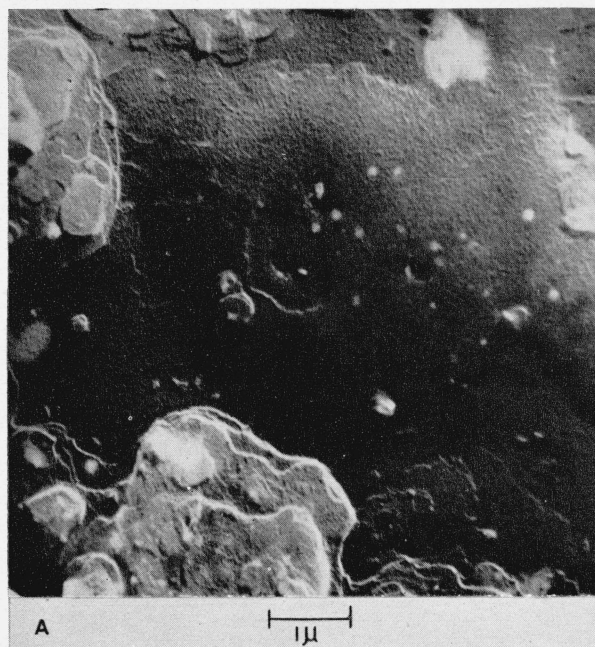
FIGURE 5. *Rubidium palmitate*

	Total magnification	Electronic	Optical
A	10, 400	5, 200	2.0
B	10, 400	5, 200	2.0
C	35, 200	9, 500	3.7
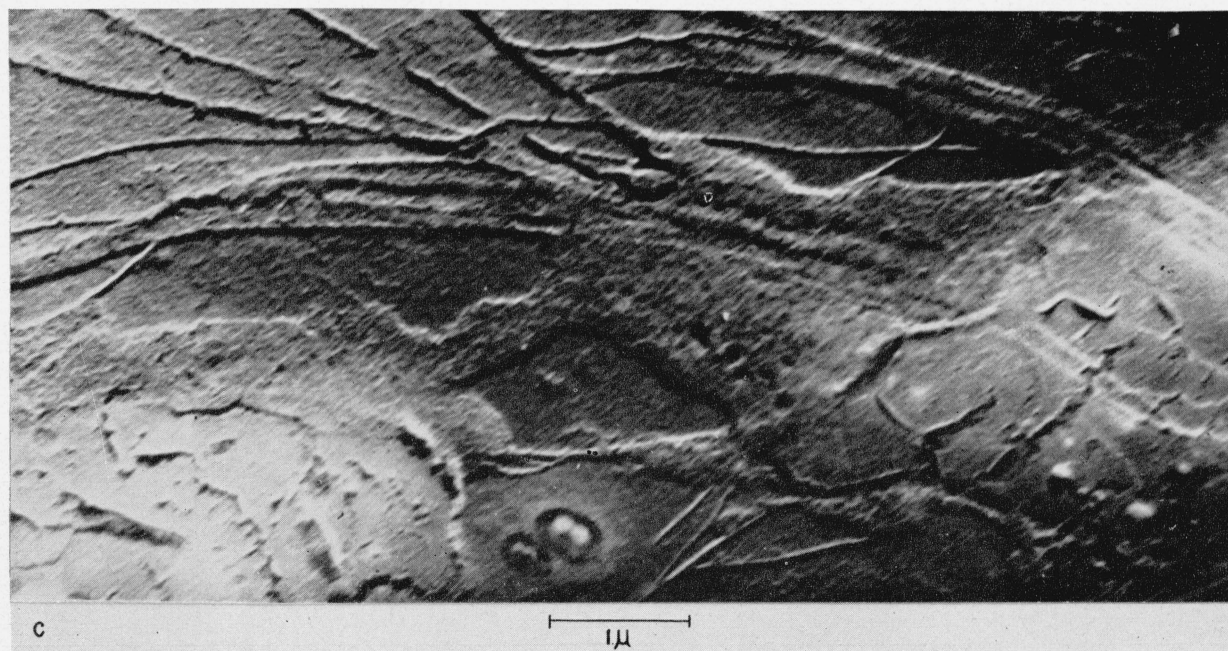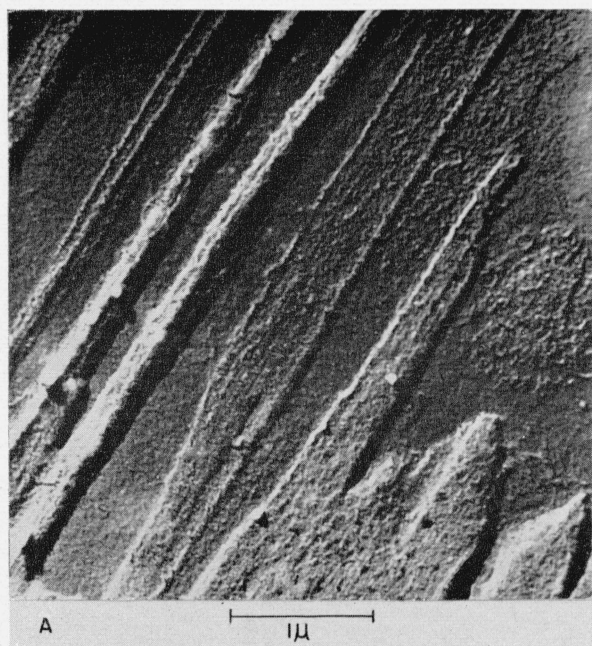
FIGURE 6.   *Cesium palmitate*

	Total magnification	Electronic	Optical
A	19,000	9,500	2.0
B	10,400	5,200	2.0
C	18,700	5,200	3.6
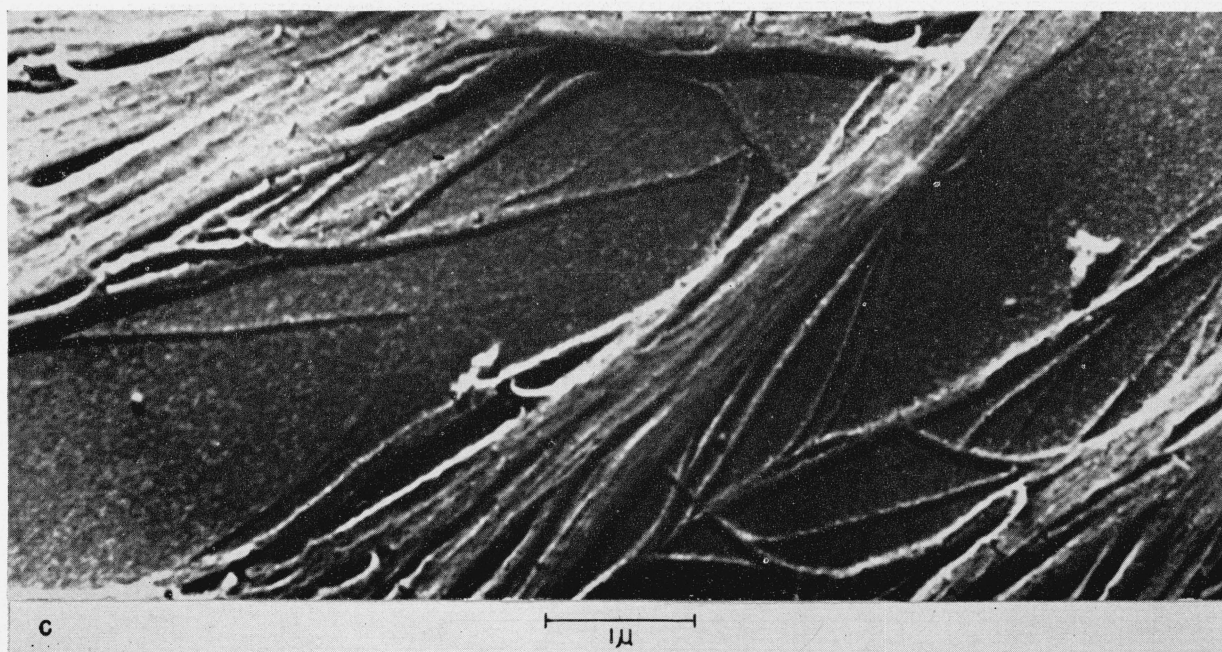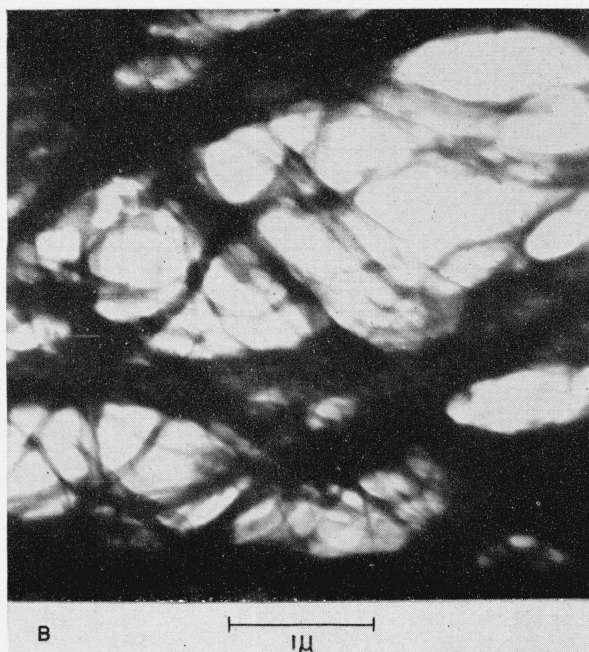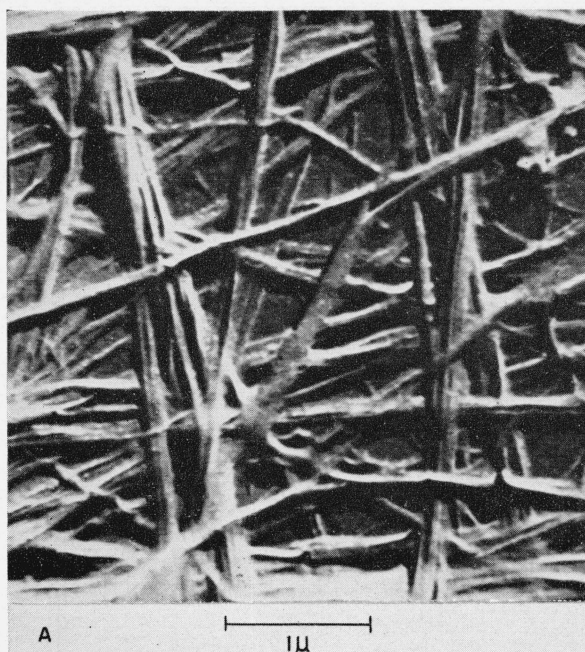
FIGURE 7. *Sodium laurate*

	Total magnification	Electronic	Optical
A	19,000	9,500	2.0
B	19,000	9,500	2.0
C	19,800	5,200	3.8
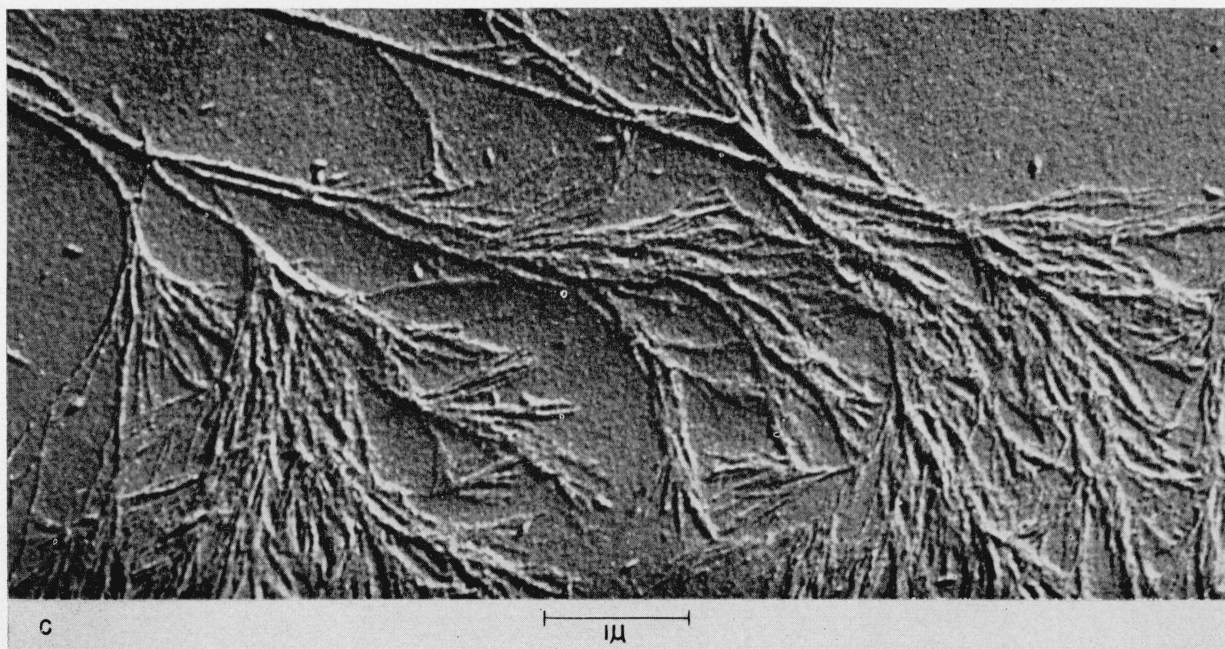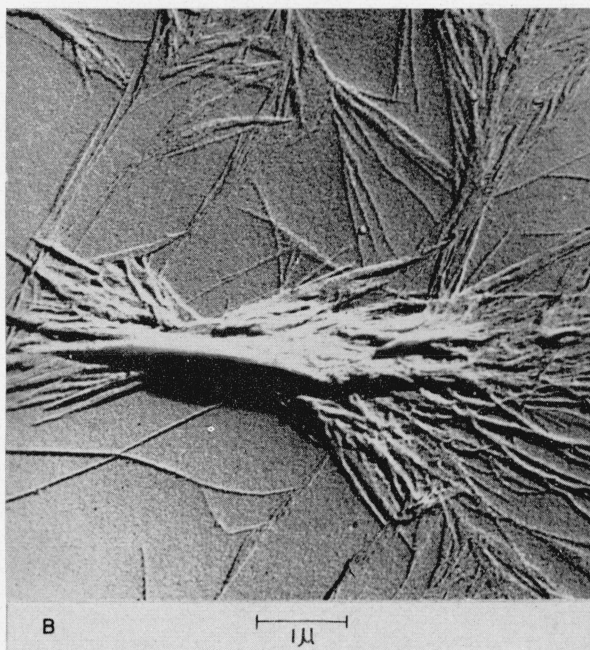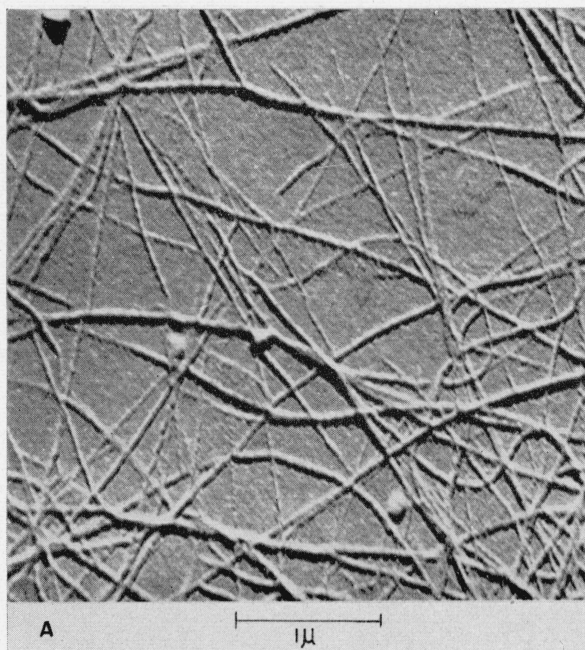
FIGURE 8. *Sodium stearate*

	Total magnification	Electronic	Optical
A	19,000	9,500	2.0
B	12,000	6,000	2.0
C	19,200	5,200	3.7
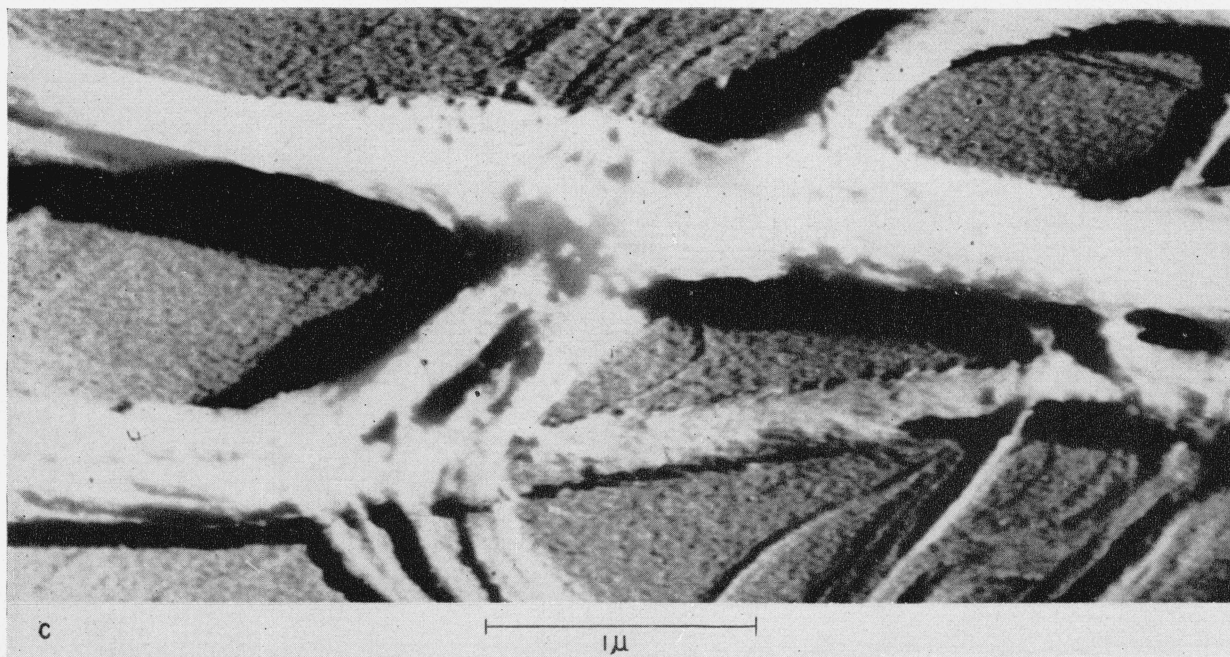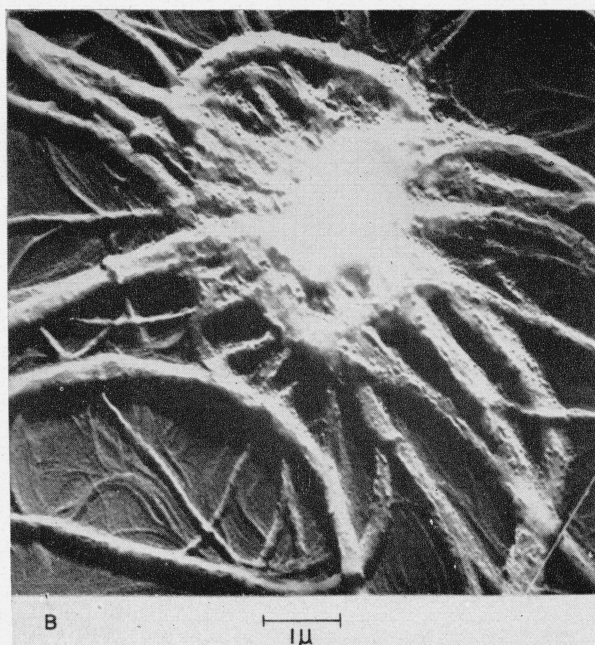
FIGURE 9. *Sodium oleate*

	Total magnification	Electronic	Optical
A	19,000	9,500	2.0
B	10,400	5,200	2.0
C	36,100	9,500	3.8
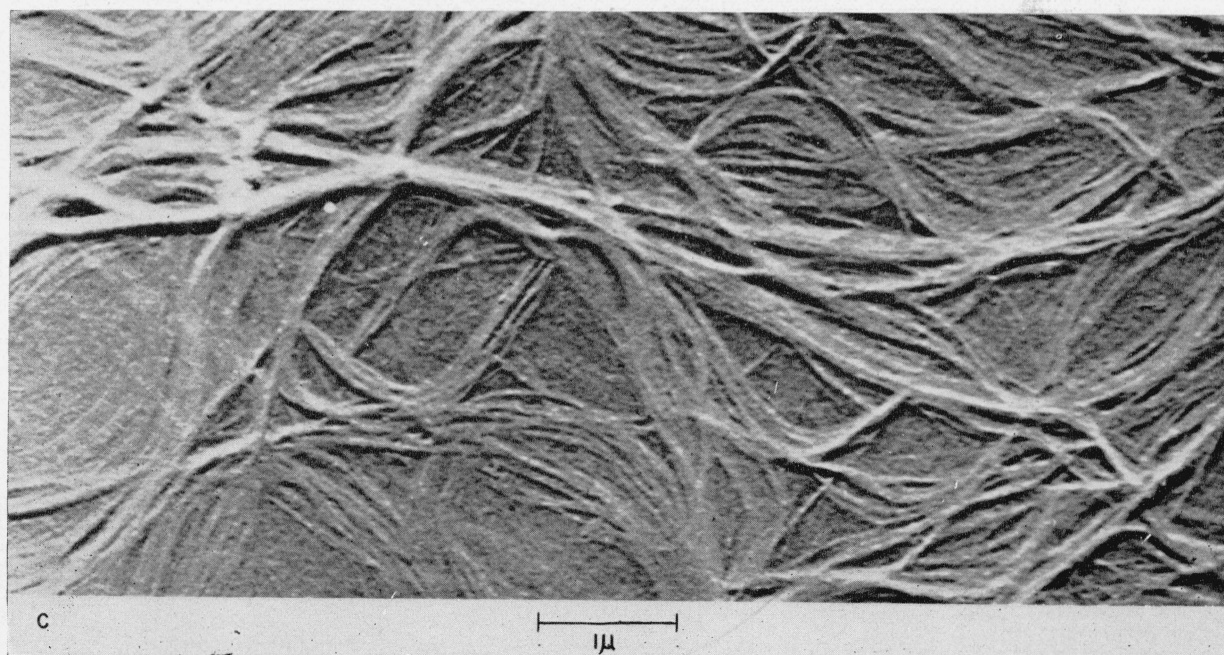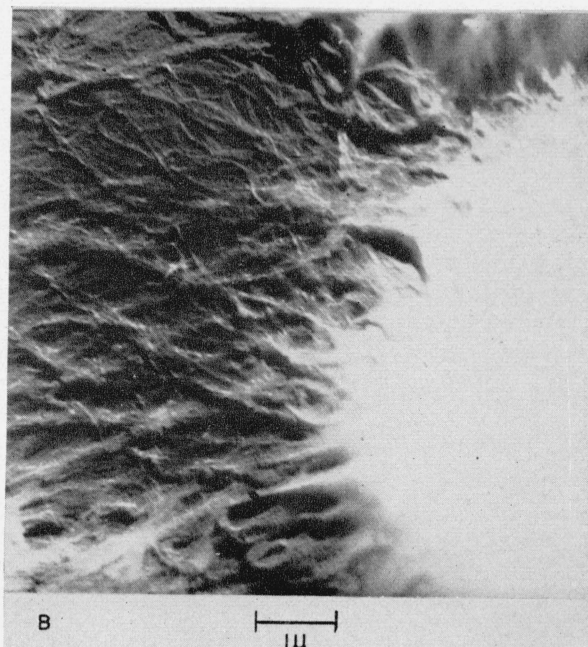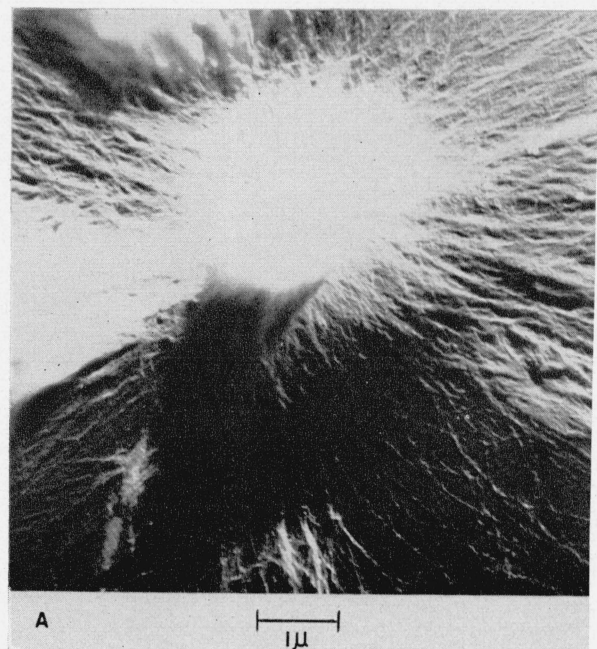
FIGURE 10. *T3 toilet soap (USA)*

	Total magnification	Electronic	Optical
A	10,400	5,200	2.0
B	10,400	5,200	2.0
C	18,700	5,200	3.6
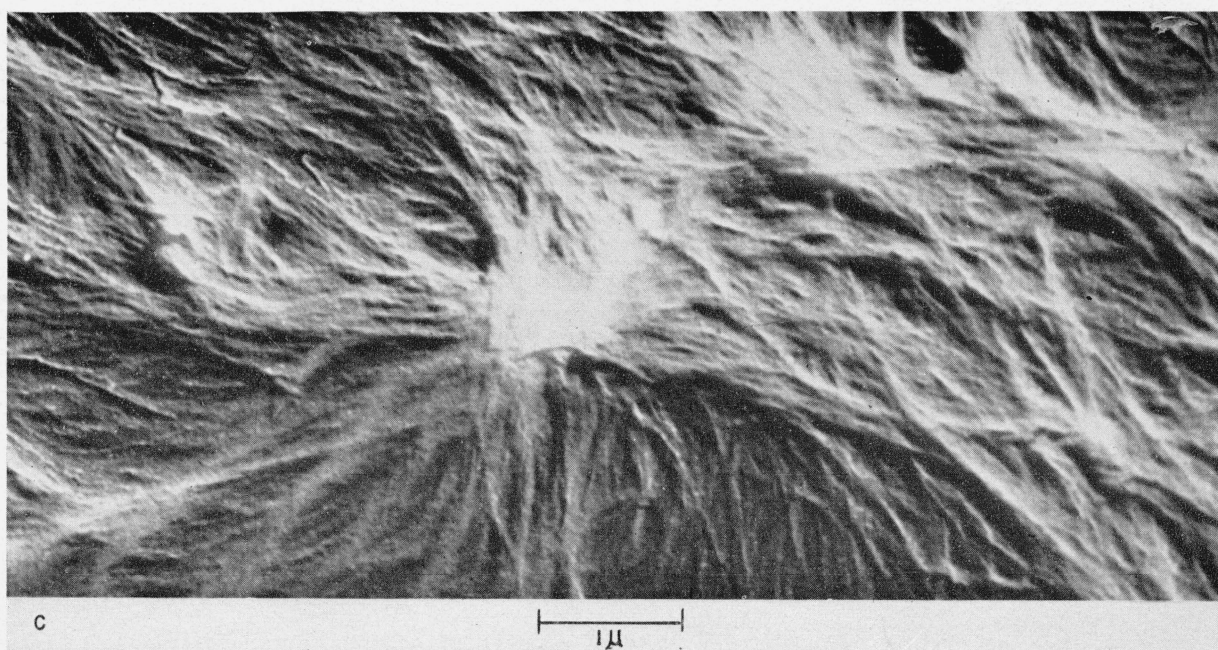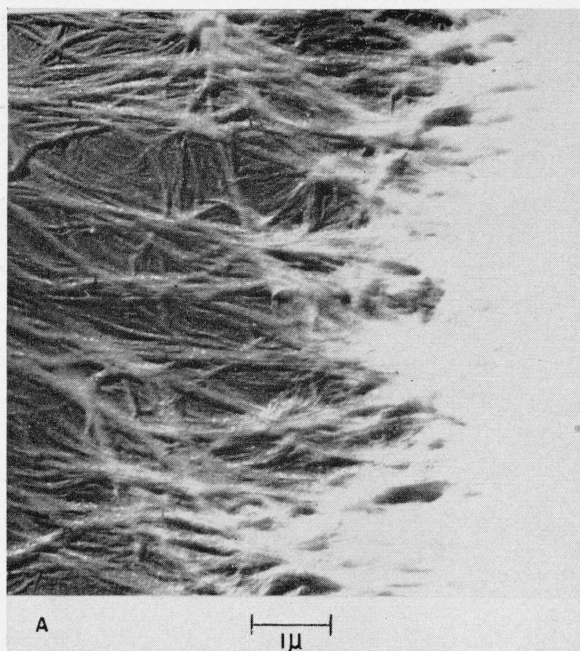
FIGURE 11. *T8 toilet soap (India)*

	Total mag-nification	Electronic	Optical
A	10, 400	5, 200	2. 0
B	21, 000	10, 500	2 0
C	19, 200	5, 200	3. 7
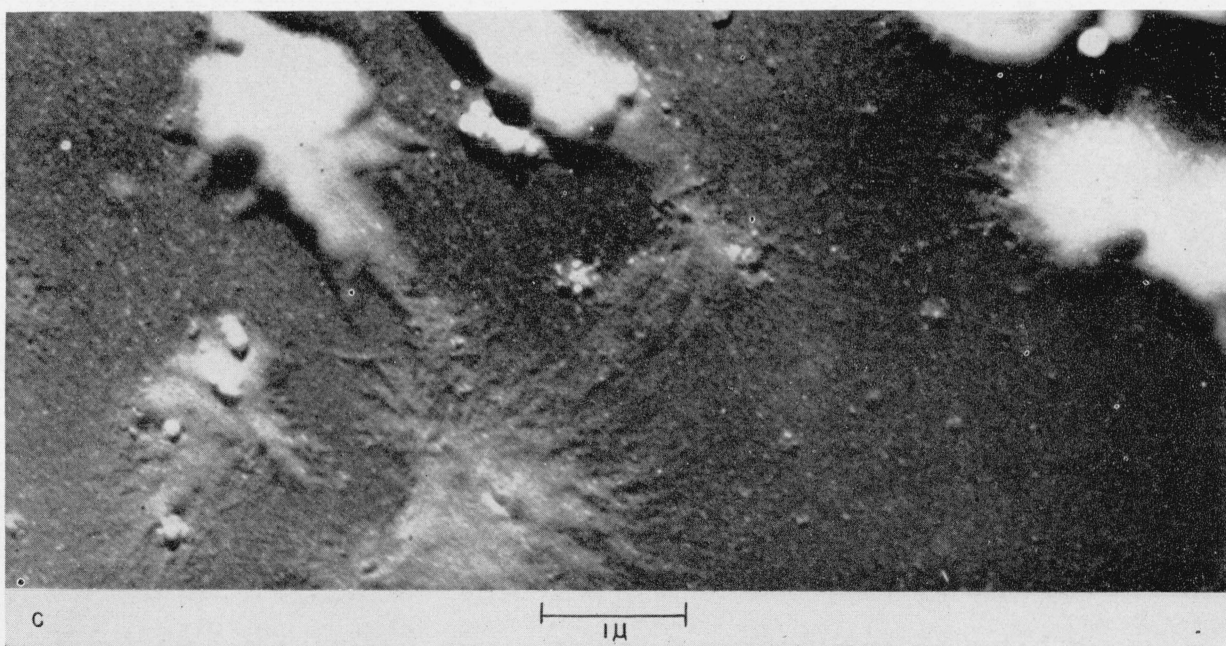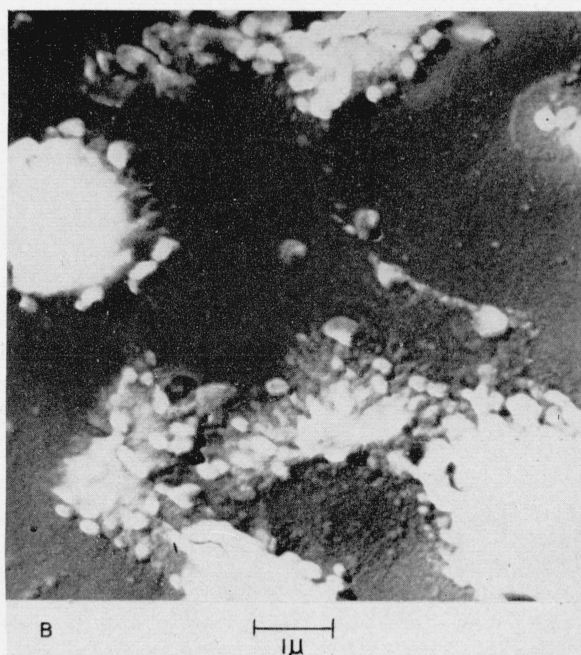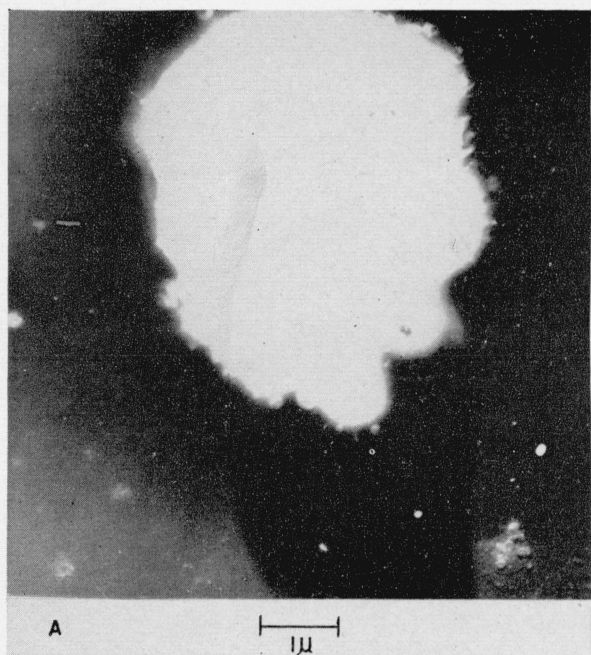
FIGURE 12.   *W5 washing soap (India)*

	Total mag-nification	Electronic	Optical
A	10, 400	5, 200	2. 0
B	10, 400	5, 200	2. 0
C	19, 200	5, 200	3. 7
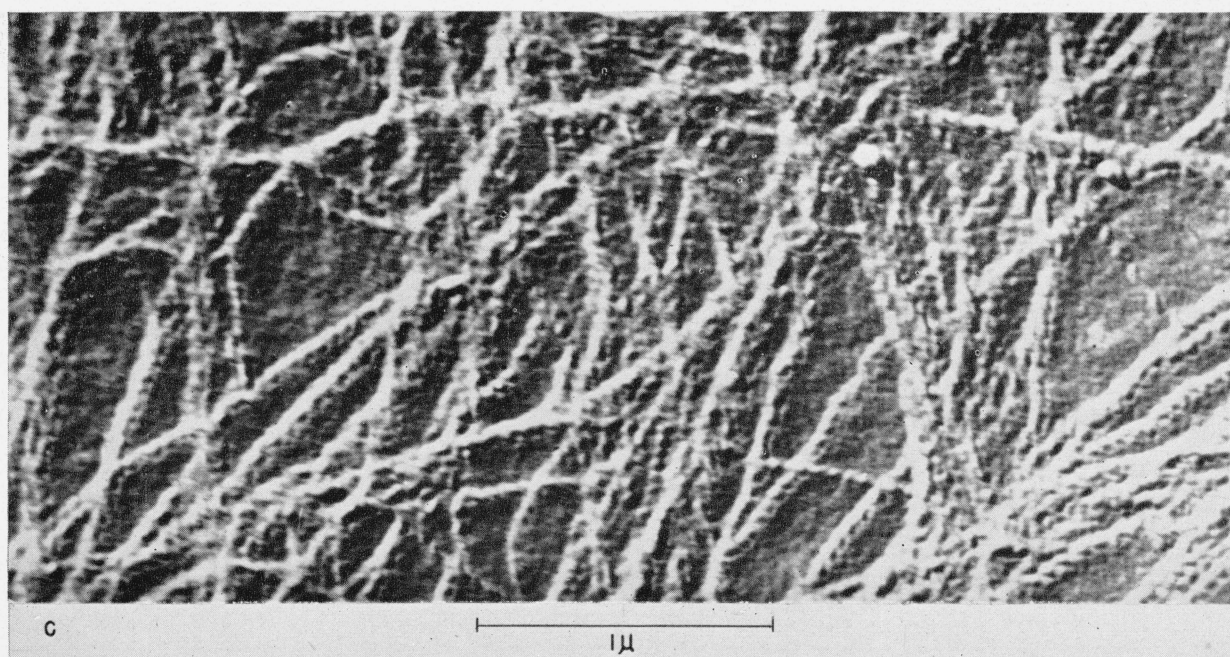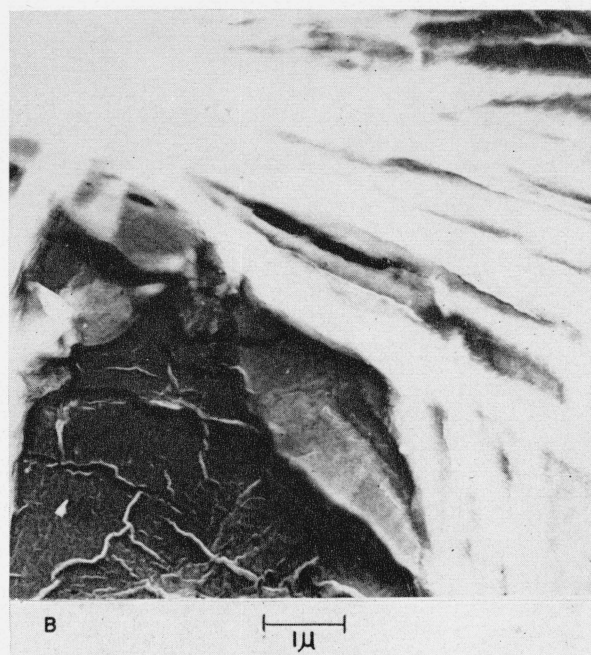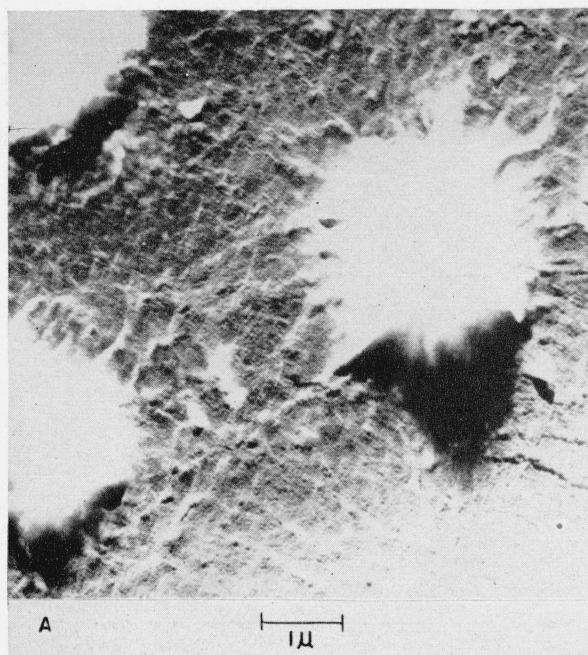
FIGURE 13. *S5 shaving soap (India)*

	Total mag-nification	Electronic	Optical
A	10, 400	5, 200	2. 0
B	10, 400	5, 200	2. 0
C	38, 900	10, 500	3. 7

WASHINGTON, December 31, 1948.