

Micrography of Tubular-Type Battery Plates

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ABSTRACT

Tubular type battery plates of various stages of production were obtained from three battery manufacturers and examined microscopically. It was ascertained that certain physical changes took place in the microstructure of the material after soaking in acid and after forming. These changes were not the same as those that occurred when plates were prepared from mixed and cured paste and subsequently formed. To all visible appearances the product from the tubular plate appeared to have cohesion and porosity equal to or better than from most pasted plates. However, the adherence of the paste to the metal spline was poor.

Of particular interest was the discovery that the formed active material of one of these manufacturers contained a definite reticulate structure such as had previously been found to coexist with plates that successfully floated without loss of capacity.

PROBLEM STATUS

This report concludes one phase of the problem; work is continuing on other phases.

AUTHORIZATION

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MICROGRAPHY OF TUBULAR-TYPE BATTERY PLATES

INTRODUCTION

The tubular positive battery plate employed in certain industrial lead-acid batteries differs from the more usually employed pasted positive both in appearance and method of manufacture. The method of manufacture used in the tubular plate indicates that in this plate the lower oxides might be converted to PbO_2 by a different process and with a resultant different microstructure than was the case in the pasted positive plate. In the usual tubular plate construction the necessary support and conductivity of the plate is provided by a series of parallel lead alloy splines positioned along a common top bar like the teeth of a comb. Each suspended lead-alloy spline is enclosed in a porous tubular container of such a diameter as to permit the dry oxide to be introduced around the spline and within the container. The required density is obtained by vibration, after which a bottom support bar is put in place which adds rigidity to the splines and encloses the lower end of the tubes. This bar may be either metal or plastic. The plates are then usually soaked in sulfuric acid solution until the electrolyte has completely penetrated. Then the lower oxide is converted to PbO_2 by the usual electrolytic process.

The heavy central metal spline and the construction of the container that surrounds each spline ensure that the active material is kept in contact with the metal and that the PbO_2 is retained within the container. Such plates find extensive use in industrial service where heavy vibration or shock is experienced.

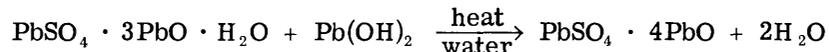
The more conventional plate used in starting, lighting, and ignition service, on the other hand, employs a continuous metal grid into the pockets of which is pasted a plastic mixture of PbO and H_2SO_4 . This mixture is usually allowed to set into a hard mass through a combined process of drying and reaction, so that the final plate is very hard and the paste mix adheres tightly between the grid members.

In the mixing of the paste and during the slow drying process one or more of the following basic sulfates are produced: monobasic lead sulfate, $\text{PbSO}_4 \cdot \text{PbO}$; tribasic lead sulfate, $\text{PbSO}_4 \cdot 3\text{PbO} \cdot \text{H}_2\text{O}$; or tetrabasic lead sulfate, $\text{PbSO}_4 \cdot 4\text{PbO}$. For convenience in expressing the reactions one may consider that PbO reacts with water to form Pb(OH)_2 , a strongly alkaline material. Although a definite lead hydroxide has not been identified in this process, the sequence can be conveniently expressed as follows:



It will be seen that increasing additions of H_2SO_4 cause the conversion of PbO first into the tribasic form, then to the monobasic form, and finally, if sufficient acid is present, to the normal lead sulfate. In the usual mixing process the amount of acid added is insufficient to reach this point, and the final mass consists of unconverted PbO , tribasic lead sulfate, and perhaps some monobasic lead sulfate.

When the temperature of such a mass is raised above approximately 60° C and water is present, a portion will be converted to tetrabasic lead sulfate, possibly according to the reaction



Thus it can be seen that the final composition of the unformed pasted plate may include any or all of these basic sulfates, depending on the amount of acid used, the temperature attained, and other conditions of mixing and curing.

In the experimental mixing of pastes one soon realizes that even a temporary excess of sulfuric acid is to be avoided, for it becomes evident that the PbSO_4 that forms as a film upon particles of PbO has the same protective characteristics for the underlying material as is the case with lead sulfate upon lead itself. As a consequence the thus protected PbO remains unaltered in subsequent mixing. In addition, the PbSO_4 once formed does not again easily convert to one of the basic oxides when the temporary excess of H_2SO_4 is removed and the pH again shifts toward the alkaline end of the scale.

It can thus be seen that the process in the tubular plate could differ considerably from that outlined for the pasted plate. The soaking of the tubular plate occurs in an excess of acid and there is no curing or drying period during which crystals could grow. Very little is known as to just what does occur in the tubular plate. One would expect that a layer of oxide at the surface would become protected by a layer of PbSO_4 and that in addition a slow neutralization of the acid would occur as it percolated deeper into the section. This in turn should result in an extremely nonuniform set of reactions, producing PbSO_4 at the outer rim of the section and unpredictable amounts of the basic sulfates at various deeper levels. This condition would then contribute to a very nonuniform microstructure after formation.

This rather large difference in the steps of manufacture for the two kind of plates made the microscopic examination of tubular plates of particular interest. Similar examination had already been made of the pasted plates used in starting, lighting, and ignition, and the structure of the final plate had been found to depend almost entirely upon the method of mixing and curing.

BASIS OF THE EXAMINATION

The basis of the examination was a microscopic study. Individual splines were carefully cut from the tubular plates, leaving the container and contents as undisturbed as possible. These tubes were dried in an oven to remove all moisture and were then transferred to a vacuum desiccator. In the vacuum they were covered with an already catalyzed low viscosity liquid polyester, and while the polyester was still liquid they were subjected to atmospheric pressure. When the polyester had hardened, sections were cut at right angles to the length of the tube to expose cross sections of tube, active material, and the alloy spline. After mounting and suitable polishing these sections were examined microscopically.

Samples from three manufacturers were included in the examination and were compared in the as-filled condition (two manufacturers), after soaking, and after forming. One manufacturer also included samples formed with and without the benefit of a presoak. The samples were examined with the following points in mind:

1. Effectiveness of the tubular container in retaining the dry oxide or the formed active material.

2. Nature and appearance of the dry oxide
 - a. Particle size and range
 - b. Effectiveness of mixing
 - c. Identifiable particles
3. Changes produced by soaking
 - a. Effectiveness and extent of wetting
 - b. Chemical changes
 - c. Physical changes
 - d. Identifiable particles
 - e. Comparison with mixed and pasted active material
4. Nature and appearance of the active material after forming
 - a. Chemical changes
 - b. Physical change and structure differences
 - c. Identifiable particles
 - d. Comparison with pasted and formed plates.

As mentioned previously plates from three manufacturers were included in the examination. For two of these complete information as to the oxide composition and method used in the plate manufacture were included. Samples obtained from the other manufacturer were not accompanied by details of their preparation; in this case certain assumptions were necessary.

Samples were obtained for this study with the understanding that any information as to details of composition or method of manufacture would remain confidential, so this report will disregard such information and concern itself only with those items that could be ascertained from the microscopic examination itself.

GENERAL OBSERVATIONS

The plates obtained from the different manufacturers were not of the same overall dimensions, but the tubular containers from the different plates were found to be very close to the same diameter and to have approximately the same size and design of the internal lead alloy splines. In all other respects the plates differed markedly. Two were filled with an oxide mix evidently containing sufficient red lead (Pb_3O_4) to give the material a red or orange color, while the third contained an obviously leady oxide of a gray color. The appearance after forming showed very little difference to the unaided eye. Two of the manufacturers used tubes so closely resembling each other in material and construction as to indicate that they were the same, although the samples were obtained from widely separated geographic locations. The third manufacturer used tubes of an entirely different material and of different construction. Even the microstructure in the splines differed in each case, although all appeared to be an antimony-lead alloy.

DETAILS OF THE MICROSCOPIC EXAMINATION

The Tubular Container

Microscopic examination showed that the containers made by two of the manufacturers, which will hereinafter be referred to as manufacturers 2 and 3, were practically identical; a single description will suffice for both. The two similar containers had an inner woven material and an outer continuous plastic film pierced with numerous relatively large diameter holes. This latter material has a density and consistency evidently very near to that of the impregnating polyester and so is practically invisible when in the mounting medium. Yet this material furnishes physical restraint outside the woven container. From all visible indications this type of container is very effective in retaining the dry oxide and yet appears to be sufficiently porous to allow free passage of the electrolyte.

Figure 1 indicates the appearance of the individual fibers of the inner woven material as seen in a cross section taken at right angles to the tube length. Although not evident in this particular section it was obvious from the overall examination that these fibers were arranged in bundles that constituted individual threads and that these threads were woven together in a complicated herringbone weave that allowed very little open space between individual threads. The fibers themselves appeared to be circular when cut at right angles to the surface and assumed various oval sections when cut at other angles. Regardless of the angle the spacing of the individual fibers of a thread was very close (Fig. 1). There appeared to be no clearly defined warp and woof to the material, but the total thickness of the container wall seen in the section varied as more or less threads were exposed in different parts of the section. This is shown by a comparison of Figs. 2 and 3, taken at considerable lower magnification than Fig. 1. The maximum thickness attained by the container wall is illustrated in Fig. 2, which is taken at the junction of two or more threads.

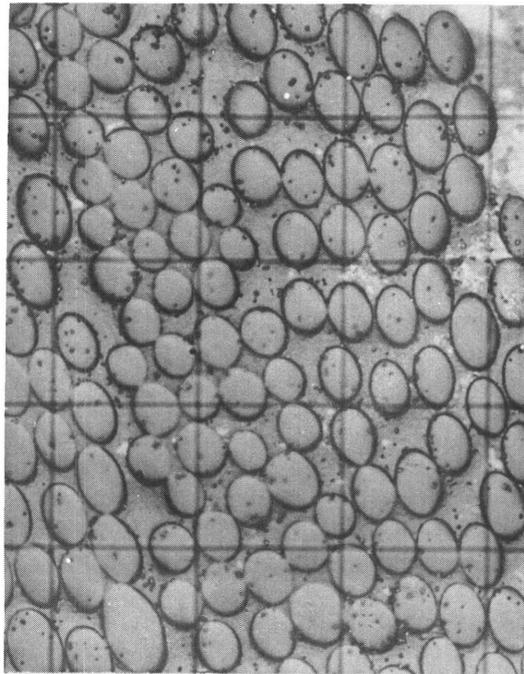


Fig. 1 - Highly magnified cross section of fibers (presumably glass) in the fabric of a tubular container used to retain oxide particles. (30-micron squares; original magnification 800X.)

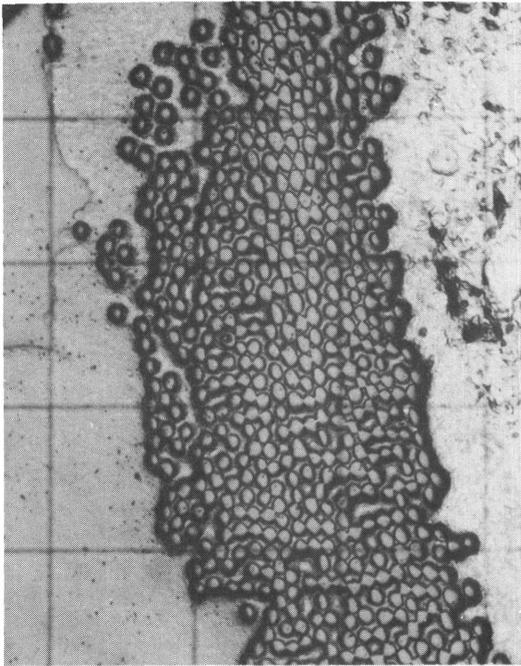


Fig. 2 - Similar to Fig. 1 but at a lower magnification to show the total thickness of the container wall at a place where two or more threads contribute to maximum container thickness. (95-micron squares; original magnification 250X.)

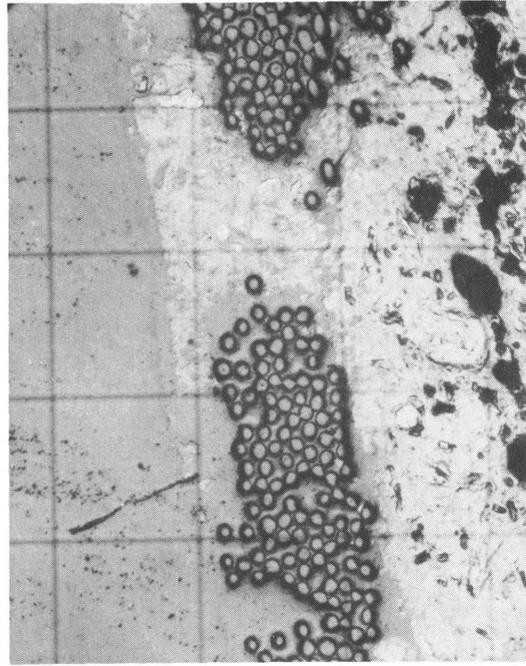


Fig. 3 - Section of container wall similar to Fig. 2 but where only one thread contributes to wall thickness. The effect of mesh in the fabric is shown by the oxide particles passed through the opening but restrained by a plastic outer film. (95-micron squares; original magnification 250X.)

In Fig. 3, on the other hand, only one thread width is shown. The open space represents about the maximum that this type of weave permitted, and even this amount was seen very seldom in any of the cross sections. Note however that at such points the lead oxide works through the woven container wall. The almost straight boundary line shown by the oxide after shifting through the fabric (Fig. 3) is due to the restraint of the outer plastic film that is invisible in the polyester. In addition, as can be seen to the right in Fig. 1, lead oxide particles penetrate slightly between the individual fibers of each thread, but no case was found where this penetration had extended very far into the thread.

The tubular container used by the third manufacturer, hereinafter referred to as manufacturer 1, was woven quite differently, was composed of a different material, and was apparently used without the thin, multiholed, outer plastic film. A cross-sectional view of the fibers appears as in Fig. 4, and no angle of cutting produced oval or circular sections as seen in the previous illustrations. As in the previous case the proximity of individual fibers of the thread to one another appeared to be effective in retaining the dry oxide and yet permit the passage of electrolyte. In this case however there was a distinct warp and woof to the material; the cross section at its thickest point appeared as in Fig. 5. It can be seen that there is a thread perpendicular to the plane of the photograph, around which is looped one parallel to the plane. Where the parallel threads lay one upon another, there was apparently a rather open spacing, as areas such as shown in Fig. 6 were quite common. In such a cross section there was presumably a thread parallel to and above the plane of the section and another parallel to but immediately below the section. In the plane of the photograph the lead oxide was free to shift through. Such openings would not seem to be advantageous.

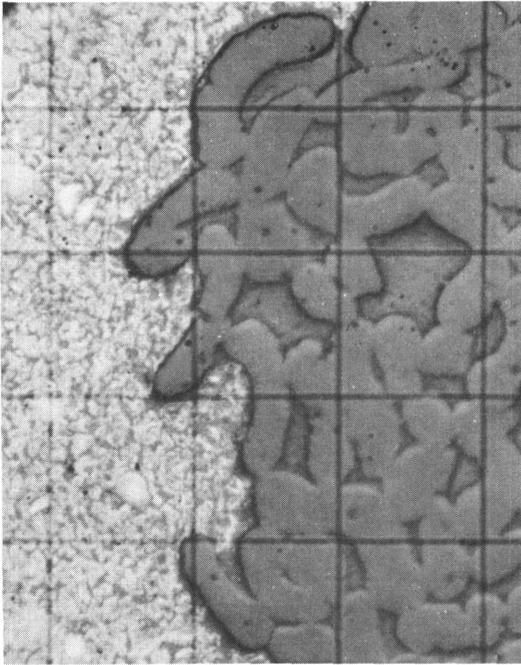


Fig. 4 - Cross section (magnified the same as Fig. 1) through the fibers of a single thread of an unidentified plastic material used as the fabric of tubular container. This container has no plastic outer film such as made itself evident in Fig. 3. (30-micron squares; original magnification 800X.)

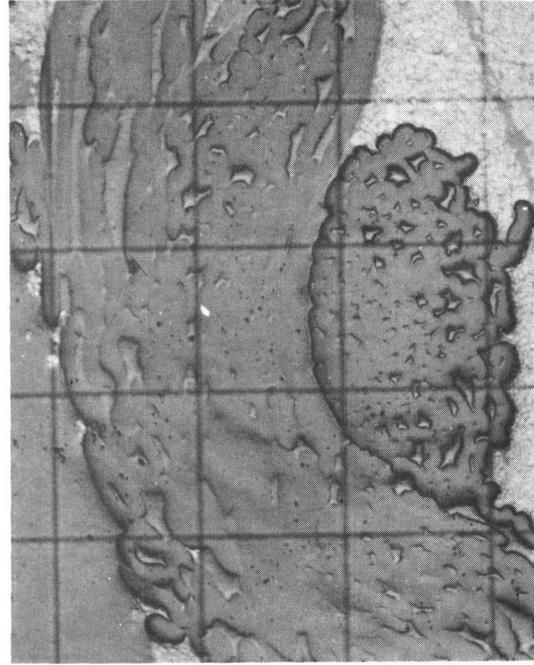


Fig. 5 - Fibers of the plastic material shown in Fig. 4 but at lower magnification to show the warp and woof of the material and the manner in which the oxide is maintained. This view shows the fabric at the thickest point, where threads overlap. (95-micron squares; original magnification 250X.)

Although microscopic characteristics indicated that the two first mentioned tubes contained fibers of the same material, consisting of what appeared to be glass, and that the last was of a quite different plastic material, no attempt was made to identify either.

Appearance of the Material in the Tubular Containers

The oxide used in the positive tubular plate of manufacturer 1 was dull orange in the dry state. Although a few particles of lead were detected in the mix such as that shown by the arrow in Fig. 7, this material would not be considered a leady oxide. With vertical illumination the range of particle sizes can be seen and Fig. 7 is representative of what is found. It can also be seen from the figure that the particles are packed rather closely with relatively little space between them, as the smaller particles fill the spaces between the larger. When this material is viewed by polarized light, only a reddish glare is visible. However, the use of a green filter in addition to polarized lighting gives an appearance illustrated by Fig. 8. Careful inspection reveals that dark areas in Fig. 8 match some of the particles seen in Fig. 7. These particles were deep orange under polarized light. Many of the other particles seen in Fig. 7, however, merge into the background as seen in Fig. 8; these particles had less intense and more uniform color. Neither method of illumination suggested that the particles had a definite crystalline regularity. The oxide appeared to consist entirely of Pb_3O_4 although PbO could probably be present in considerable amount without microscopic detection.



Fig. 6 - Same fabric as in Fig. 5 but here shown at the thinnest point. The mesh here is large, and particle loss is extensive. (95-micron squares; original magnification 250X.)

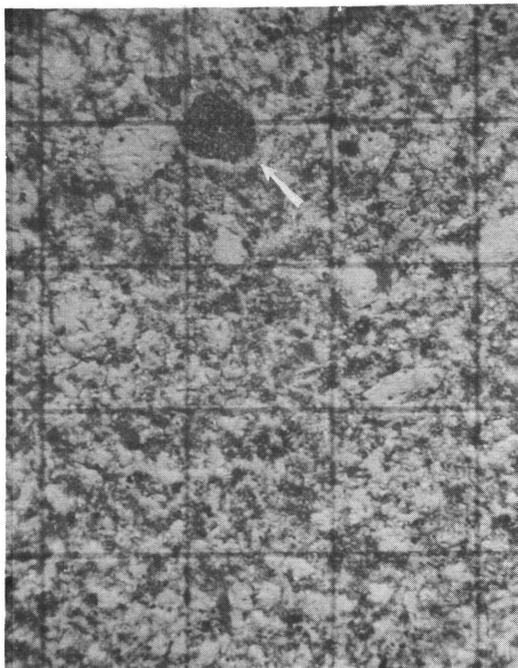
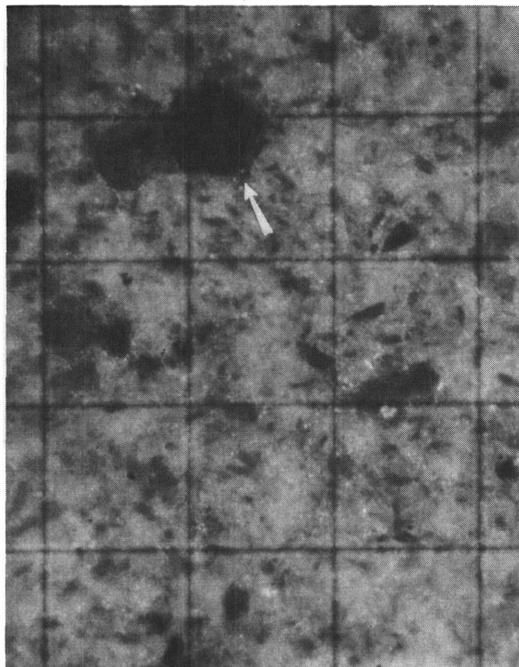


Fig. 7 - Appearance (under vertical illumination) of oxide particles as seen in the as-filled condition for manufacturer 1. A lead particle is shown by the arrow. Light areas are particles of red lead (Pb_3O_4), while dark areas represent the impregnating plastic. (30-micron squares; original magnification 800X.)

Fig. 8 - Same field of view as shown in Fig. 7 but here shown by polarized light plus a green filter to remove an overall reddish glare. Background particles were in almost uniform pale yellow under this condition, while the few dark particles in the photograph were deep orange. (30-micron squares; original magnification 800X.)



Quite different was the oxide mix used by manufacturer 2. In this case the oxide was predominantly gray, although areas of yellow and orange appeared at certain points in the cross section. This appeared to indicate that mixing had not been thorough. One of the largest such unmixed areas is shown in Fig. 9; it was orange and appeared to consist entirely of one constituent. The material in this area appeared to be similar to that used by manufacturer 1 (see Fig. 7). A portion of the light area of Fig. 9 is shown again in Fig. 10 but at the same magnification and type of illumination used for Fig. 7.

In most of the oxide mix used by manufacturer 2 the orange constituent had been thoroughly blended with another principal constituent which appeared to be a leady oxide. The resultant structure, which was characteristic for the blended portion of the samples from this manufacturer, is shown in Fig. 11. It should be noted that the magnification used in Fig. 11 is quite a bit lower than used for Fig. 7 and that these leady oxide particles are quite a bit larger than those of oxide 1. Each of the large, approximately spherical particles in the photograph surrounds a core of lead. Each particle of leady oxide is surrounded by small particles similar to those of Fig. 10 and with the characteristics of Pb_3O_4 . In Fig. 12 this same area is shown as it appears in polarized light. It can be determined that the black filaments of lead seen in this photograph correspond to the locations of the spherical particles seen in Fig. 11. Unfortunately the rare beauty of such a field of view cannot be captured on black and white film. Each particle of the lead oxide is surrounded by individual and separated particles of orange colored oxide which form a bright border for the oxide. Also unfortunate is that the leady oxide particle, which appears light gray except for its black lead core, and the orange particles of Pb_3O_4

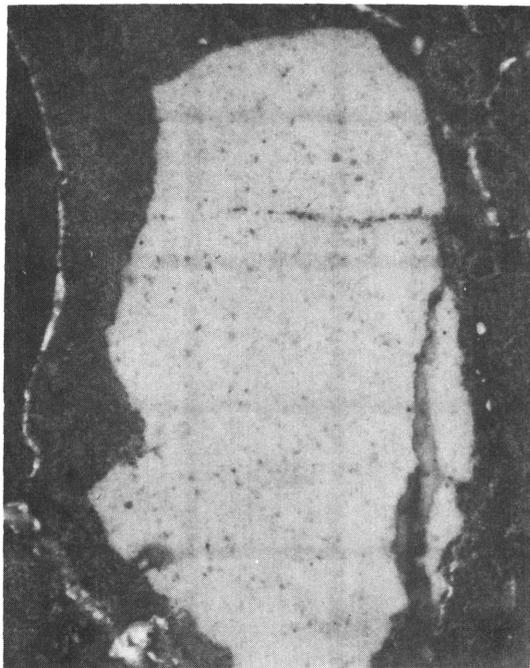


Fig. 9 - An example of an area in the tube of manufacturer 2 where mixing between the two oxides had not occurred. The view is shown as it appeared by polarized light, and the light area was orange. (528-micron squares; original magnification 45X.)

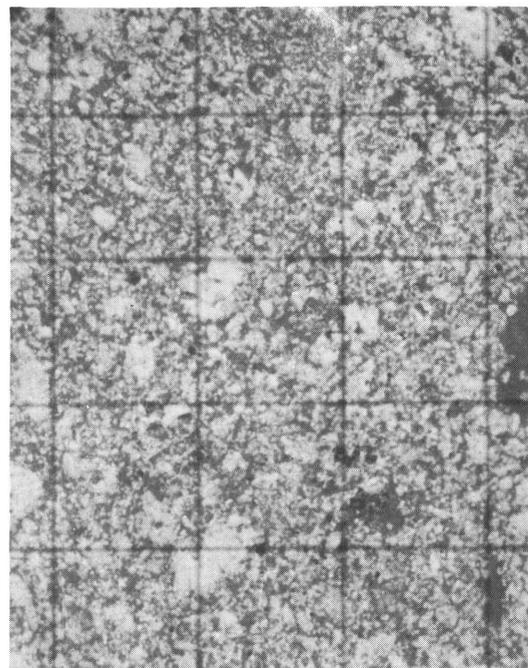


Fig. 10 - A portion of the light area in Fig. 9 at higher magnification showing the appearance and distribution of particles. The particles appear to be red lead, similar to those in Fig. 7, which is at the same illumination and magnification. (30-micron squares; original magnification 800X.)

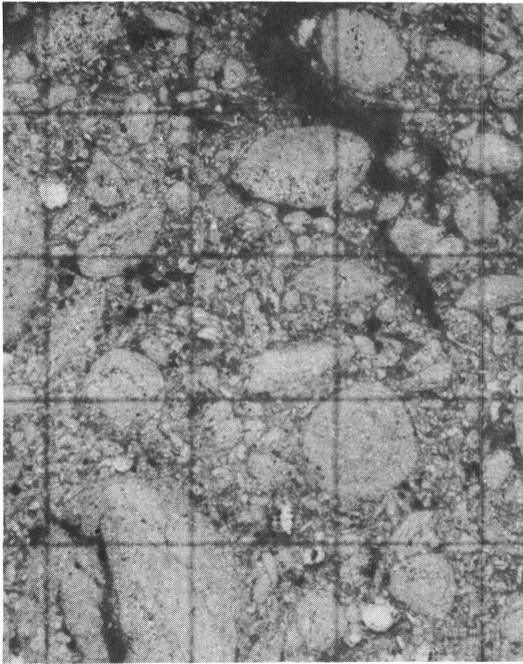


Fig. 11 - Appearance of a typical mixed portion of as-filled material in the tube of manufacturer 2. The magnification is low to include a sufficient area to indicate the range of particle sizes present. Note the very large spherical particle in the lower left corner (with a dark streak of lead) and also the more numerous much smaller spherical particles of leady oxide. The material scattered between the leady oxide is same as in the unmixed portion (Fig. 10). (95-micron squares; original magnification 250X.)

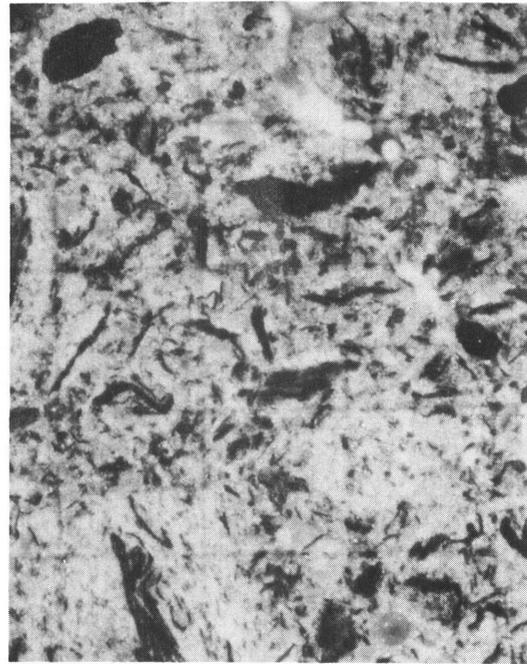


Fig. 12 - Same area as in Fig. 11 but as seen by polarized light. The dark filaments in this photograph are the lead cores of the particles of leady oxide. The white appearing background contains many light orange particles. (95-micron squares; original magnification 250X.)

photograph with almost the same density when polarized light is used. When vertical illumination is used, the Pb_3O_4 particles appear brighter and more reflective than the matrix, but this contrast also seems to be reduced in photography.

Examples of the appearance of this oxide mix when brought to the same magnification as Fig. 7 are shown in Figs. 13 and 14. In Fig. 13 the individual particles of the leady oxide can be seen clearly by vertical illumination. The shiny filament that appears to bisect each spherical particle is the hard lead core. The much smaller particles of the Pb_3O_4 can be seen in the spaces between the leady particles. Several of the rather large particles of the Pb_3O_4 in the photograph show the greater brightness associated with such material. Reference to Fig. 14 locates these same points as slightly darker areas, actually orange. The most notable of these is shown by the arrow in both Fig. 13 and 14. It must be realized that the polarized light photographs are but poor substitutes for the actual view with each particle sharply outlined by small color differences.

Manufacturer 3 did not submit samples prior to soaking, but samples of the oxide used were furnished, and there were areas in the soaked samples where the acid had not penetrated. From the appearance of these areas and of the original oxide it was determined that the dry oxide in the tube was similar in most respects to the Pb_3O_4 used in

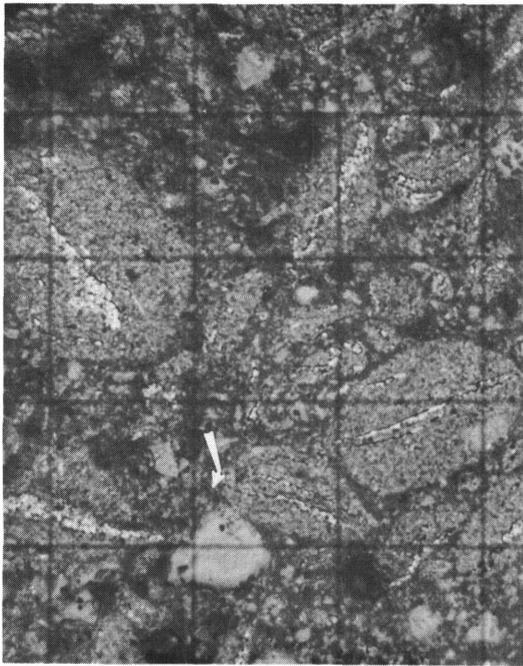


Fig. 13 - A portion of the mixed oxide of manufacturer 2 at somewhat higher magnification than Fig. 12. Note the appearance of the approximately spherical particles of the leady oxide and the small particles of red lead that surround them. The shiny filament that bisects each particle of leady oxide is the lead core. The arrow shows an unreacted Pb_3O_4 particle. (30-micron squares; original magnification 800X.)

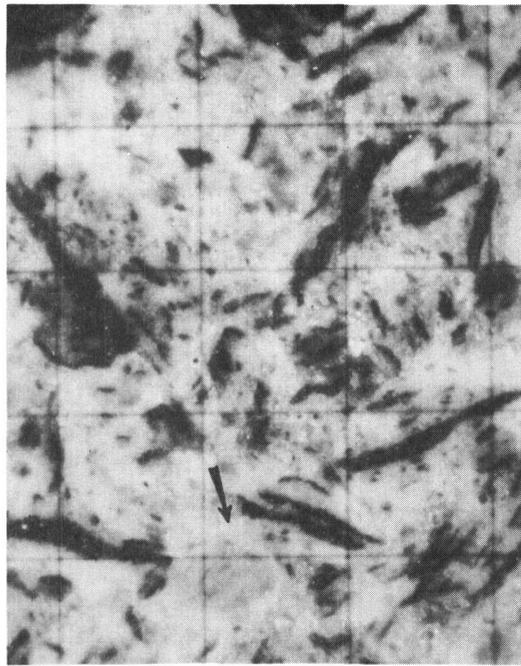
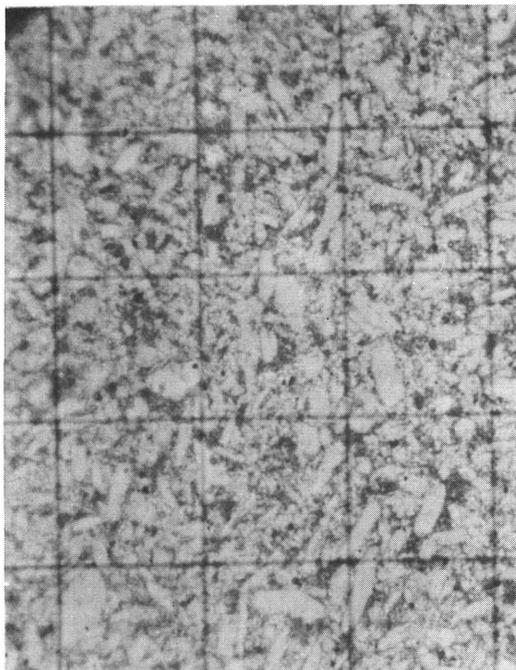


Fig. 14 - Same area as shown in Fig. 13 but as seen with polarized light. Compare with Fig. 13 to determine the relative positions of the lead cores and the boundaries of the leady oxide particles. The area surrounding each lead particle and corresponding in shape to the leady oxide particle is gray, while the areas corresponding to the spaces between the leady particles are filled with bright orange particles. In the black and white photograph, however, careful inspection is required to separate the areas. (30-micron squares; original magnification 800X.)

samples 1 and 2. The material was deep orange, definitely not a leady oxide, and from its characteristics was judged to consist entirely of red lead. Its general appearance is shown in Fig. 15. Comparison with Figs. 7 and 10 show considerable similarity but show a different distribution of coarse and fine particles, a much greater regularity of particle shape, and a more regular crystal form. The density appears to be comparable with the other two, being about the same as that shown in Fig. 10 but perhaps less than that of Fig. 7. It is well to recall, however, that Fig. 10 represents an unmixed portion of the total oxide mix used by manufacturer 2 and is by itself not representative of his product. An independent observation was that product 2 showed less tendency to pack in the tubular container than the other two and thus gave the impression of being the least dense when the tube was cut without impregnation. However, product 2 was the most difficult to impregnate with plastic, a factor that might be attributed either to a greater density or to nonwetting characteristics between the oxide and the polyester.

Fig. 15 - Oxide particles as they appear in the tubular plate of manufacturer 3. Comparison with Figs. 7 and 10 indicate that these particles are more uniformly sized and shaped. (30-micron squares; original magnification 800X.)



The Tubular Plates After Soaking in Acid

An essential step in the manufacture of tubular plates appears to be the necessity of an acid presoak to allow the acid time to penetrate into the tightly packed dry oxide and perhaps to cause a necessary conversion of the oxide to sulfate before forming is attempted.

It is not quite clear as to whether this was the purpose of the presoak from manufacturer 1. The sample marked as soaked was certainly subjected to an acid treatment of some sort, but the effect that this treatment had extended on the average less than a millimeter into the sample. Moreover the formed sample of this material showed a marked difference in microstructure between a 1-millimeter outer zone and for the remainder of the sample. This is mentioned because it was suspected that the sole purpose of the soak may have been to set the oxide and prevent loss of oxide particles through the fabric of the container during subsequent fabrication. Whatever the intention the soaking period was obviously too short to accomplish complete wetting of the sample.

Examination disclosed a definite change in color where the acid had reacted. To the unaided eye the reacted portion appeared as a continuous brown layer with a few projections of deeper penetration. Under the microscope the appearance was somewhat different. As seen by vertical illumination the reflectivity of particles in the reacted area was less than that in the unreacted portion. When viewed without a filter the reacted portion appeared dull gray, whereas the unreacted portion had an orange tint. The shape of the particles appeared to be the same as before treatment, but the outlines were somewhat fuzzy; the impression was that the acid had penetrated the particle so that in some cases it had been completely converted while in others a core of the original material was still present. Figure 16 is an example of the appearance of the soaked portion as it appeared by vertical illumination (compare with Fig. 7). A few of the larger particles appear to be unchanged, yet the reflectivity of these particles seems higher than before reaction. It is probable that this higher reflectivity is due to the formation of PbO_2 .

Examination under polarized light revealed additional changes. Where previously no detail had been visible without the use of a green filter (see Fig. 8), now detail was plainly visible and the contrast was much higher. At the outer border of the layer where the acid had penetrated (next to the tubular container) a large number of crystals had formed which were predominantly light yellow or white. Mixed among these were many much darker red or brown crystals (PbO_2). The latter were not present in such great numbers however as to explain the overall deep brown seen by the unaided eye. This is illustrated to some extent by Figs. 16 and 17, both of the same area and at the same magnification. Figure 17, taken by polarized light, indicates by the darker portions those particles that were brown or dark red. The background, which the photograph would suggest was made up entirely of white particles, actually contains a mixture of white, light yellow, and some pale reddish particles. One unreacted lead particle appears at 1. It was determined that particles giving high reflectivity when viewed by vertical illumination appeared to be of two different types when viewed by polarized light. One, such as that which appears at 2, shows as a deep red or brown particle when viewed by polarized light and probably is PbO_2 . The other, such as that at 3, is a brilliant white particle and is no doubt one of the sulfates.

As the viewpoint was shifted further toward the inner limit to which the acid had penetrated, the number of white crystals decreased; near the furthest extent of acid

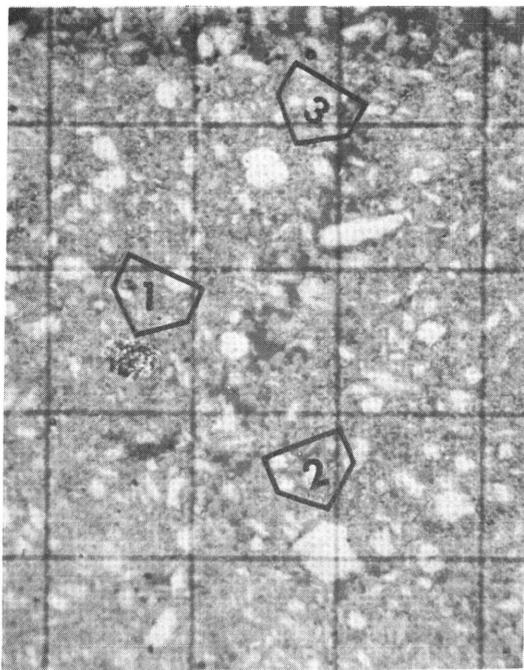


Fig. 16 - Effect of acid soak on the oxide used by manufacturer 1. The acid had penetrated to this portion of plate. Note that in comparison to Fig. 7 only a few highly reflective particles remain in a matrix of much less reflective material. (30-micron squares; original magnification 800X.)

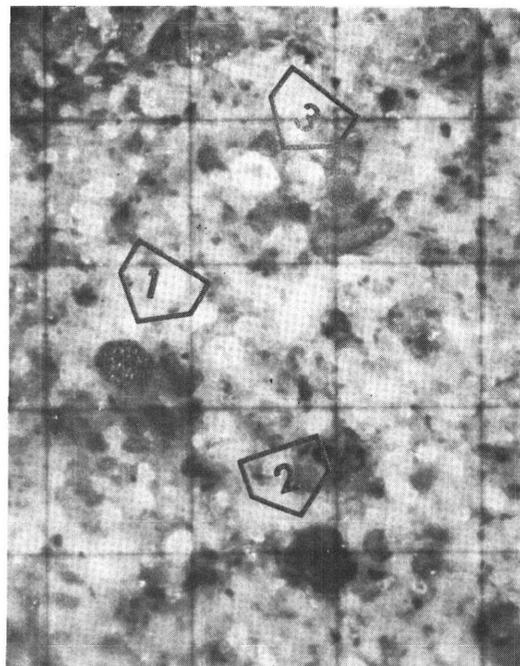


Fig. 17 - Same area as Fig. 16 but as viewed by polarized light. Two types of crystals stand out from the rest, those that are quite white (such as at 3) and those that are deep red (such as at 2). Intermediate crystals are pale yellow. The white and the red crystals both give high reflectivity under vertical illumination (Fig. 16). These are believed to be PbSO_4 and PbO_2 , respectively. (30-micron squares; original magnification 800X.)

penetration the matrix assumed a brown color, presumably from very small crystals not individually discernible. Discernible particles were almost all translucent, and decidedly white particles were infrequent. On the other hand, when this area was viewed by vertical illumination, all the highly reflective areas were found to correspond to white or very light yellow particles and none were found to be due to the deep red particles.

The soaked sample from manufacturer 2 appeared to be a metallic gray or even black rather than brown as in the previous case. Here also the soaking did not appear uniform, although the apparently unsoaked areas were rather small. These apparently unsoaked areas were orange and were scattered throughout the cross section; they appeared as large as or larger than the unmixed areas seen in the as-filled sample from this manufacturer (Fig. 9). It was first thought that these apparently unsoaked areas might be the unmixed material, but this was not the case. The orange for these apparently unsoaked areas was not as intense, and there was definite evidence of wetting and reaction, so that these areas were abnormal rather than unsoaked. Under the microscope the original structure for these abnormal areas appeared to have been the mixture of large leady particles and smaller red lead particles normal for this sample (see Fig. 13) with the remarkable difference that in this case the leady particles appeared to have swelled and burst and the core of lead to have dissolved (Fig. 18). This is confirmed by examination with polarized light (Fig. 19), which not only showed that very little lead remained in these abnormal areas but also that an unusually large number of red crystals were concentrated here and that these were unusually large in size. Further examination disclosed that these abnormal areas were enclosed by a ring of very large sulfate crystals with well developed faces.

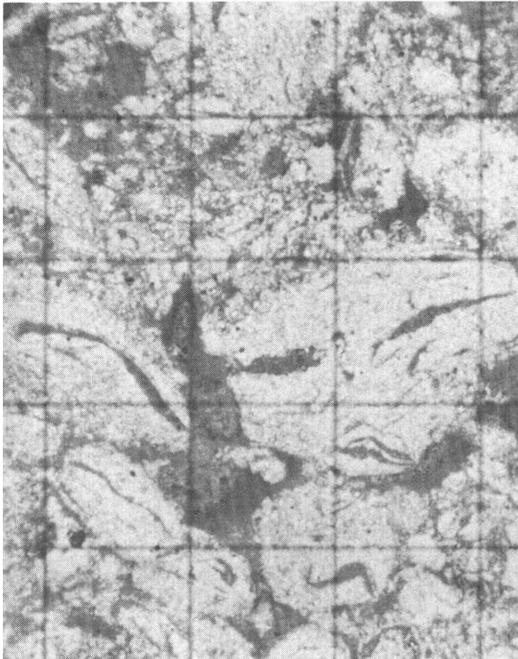


Fig. 18 - Abnormal area in the acid soaked plate of manufacturer 2. Note that the structure indicates a normal mixing of the leady oxide and the red lead but an abnormal swelled appearance of the leady oxide pellets and an absence of the lead cores. (30-micron squares; original magnification 800X.)

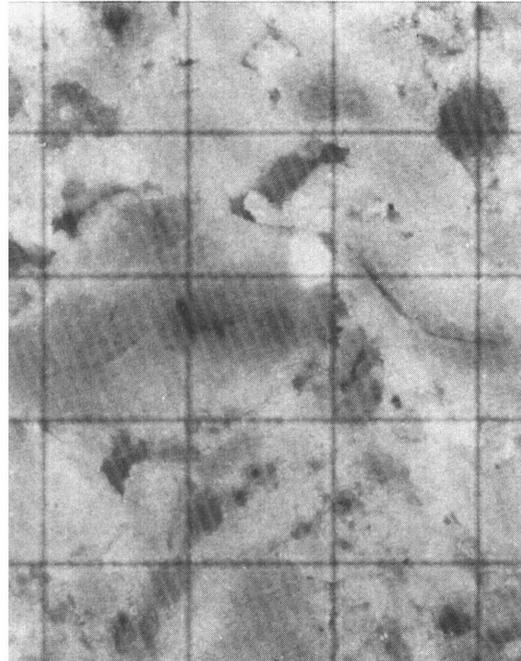


Fig. 19 - Same area as Fig. 18 but as seen by polarized light. Note the absence of lead cores. The prevalent dark areas denote unusually large numbers of large red particles, which was not indicated in Fig. 18. (30-micron squares; original magnification 800X.)

It is evident that these unusually colored areas have been wetted and that reaction has taken place. The disappearance of the lead from the leady oxide and the very large sulfate crystals surrounding the area might be indicative of an alkaline condition at this point, but the reason for it is not clear. A possible explanation is that these areas may have been surrounded by areas of unusually high density, so that they were not wetted until all other portions were reacted and the acid strength was low. However, the areas in question seem to show more than usual porosity, and no abnormality was noted in the appearance of surrounding areas. The concentration of very large sulfate crystals surrounding this area also suggests the possibility of air or gas entrapment.

The appearance of the normal areas of this sample was quite different from the above. In the normal reaction with sulfuric acid the original leady oxide granules were converted into a mass of small white crystals, closely compacted in the position of the original granule but with less distinct boundaries. The majority of the smaller particles of red lead that originally surrounded the leady oxide granules in sample 2 appear to have been converted to colorless, transparent crystals of rectilinear form, although some red particles remain in rather isolated positions. Figure 20 represents the appearance of the material as seen by vertical illumination. In general the lead cores of the leady oxide particles appear to have been unchanged and unattacked by the acid. The needlelike crystals that have formed around the lead filaments in place of the original red lead vary considerably in size in different areas and in general may be just a little larger than those seen in this photograph. Figure 21, taken by polarized light but of the same area also shows considerable less lead than the average because this area was selected primarily to illustrate the change in the red lead portions without interference from lead particles. The bright particles such as that at 1 in Fig. 20 are examples of the larger remaining red particles and are suspected of being PbO_2 . The bright area at 2 is an unattacked lead particle. Corresponding areas may be compared in Fig. 21. In normal areas the lead cores of the leady oxide particles do not appear to have suffered attack by the acid.

In the material from manufacturer 2, neither the lead particles nor the red lead crystals appear to be present in sufficient numbers to cause the overall darkening observed

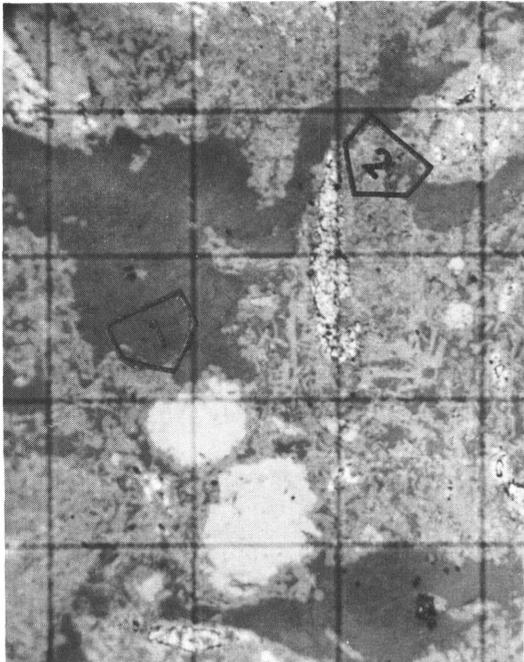
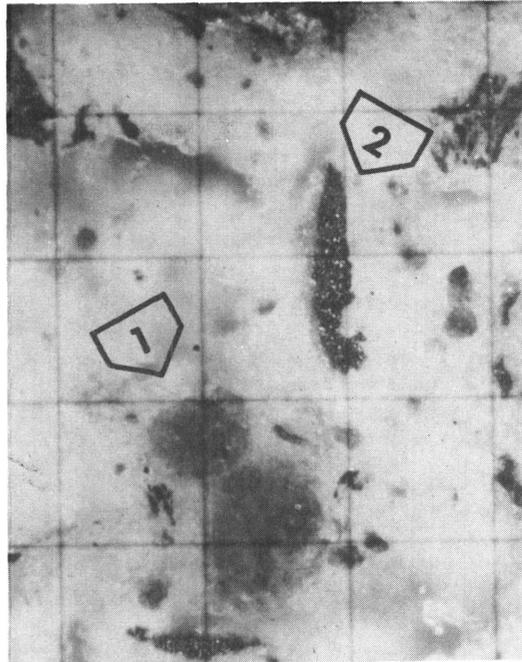


Fig. 20 - Normal area from the plate of manufacturer 2 after soaking in acid. Note the disappearance of most spherical particles, the large number of small needlelike crystals, and the lead cores, as at 2, remaining at sites of former leady oxide particles. Note also that shiny areas, as at 1, are probably red PbO_2 . (30-micron squares; original magnification 800X.)

Fig. 21 - Same area as shown in Fig. 20 but as viewed in polarized light. Compare with Fig. 20 for the location of remaining lead particles, PbO_2 , and general areas of needlelike particles not identified as such but resembling a basic sulfate crystal. (30-micron squares; original magnification 800X.)



by the unaided eye. This phenomenon of apparent darkening has been noted previously and the dark appears to depend upon the formation of many transparent, colorless crystals. Such crystals were present in this sample. Figure 22 indicates the change that occurred in the product of manufacturer 3 after the acid soak. Most particles have lost reflectivity, and it would appear that those bright particles that remain are at the core of material that has already undergone change. It was noted by reference to polarized light that, as in the majority of the cases with the other two samples, the bright particles were dark red PbO_2 . In general the same or very similar changes appeared to have taken place in all three samples after the acid soak. The main difference appeared to be in the greater transparency of the particles from manufacturer 2 and the appearance of new crystals in the former sites of leady oxide in this same material.

The Tubular Plates After Forming

One very noticeable effect of the forming process for all three plates was a definite increase in porosity as well as a slight shrinkage away from the wall of the tubular container.

The plate from manufacturer 1, as already stated, has a very different structure in the interior of the active mass than at the container face. The positions of these two different structures in the formed sample appeared to agree with positions of the areas where acid had or had not penetrated in the so-called soaked sample. Figure 23 shows the type of structure found near the center of the formed sample in the area which is assumed to have received no presoak, while Fig. 24 shows the structure that was found near the surface where the presoak almost certainly had penetrated. Figure 25, at higher magnification shows the appearance of the microstructure found near the outer portion of the active mass (Fig. 24). At this point there is no indication as to which type of structure is preferable, but it would appear that the presence or absence of the presoak is significant.

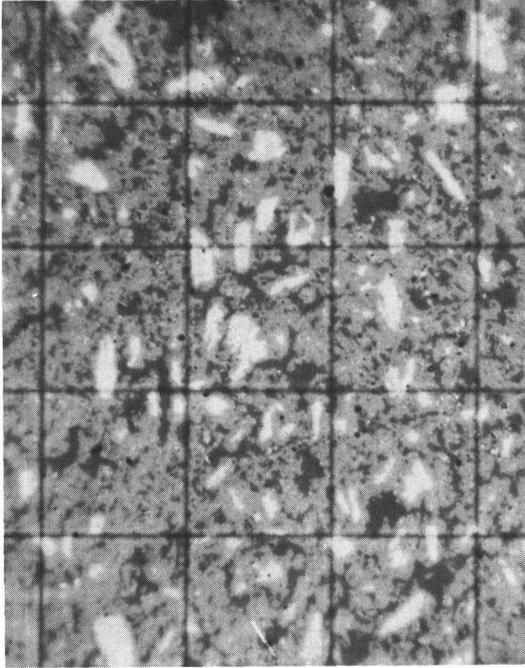


Fig. 22 - Appearance of the material of manufacturer 3 after the acid soak. Note that only large crystals are now brightly reflecting, while smaller particles show lower reflectivity. (30-micron squares; original magnification 800X.)

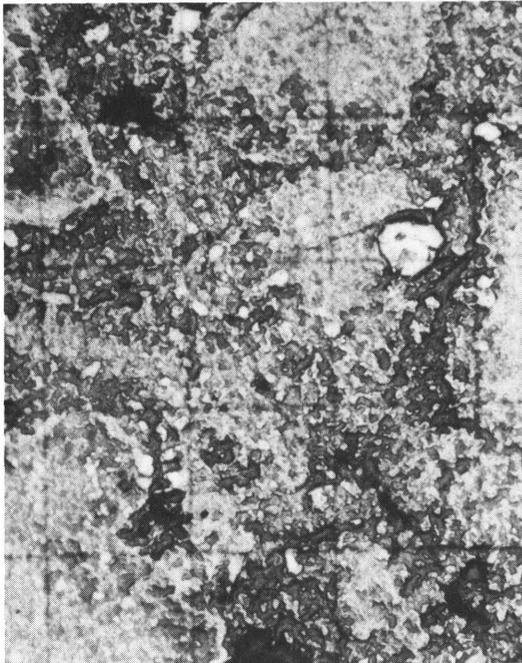


Fig. 23 - Appearance of the formed material from manufacturer 1 viewed near the center of the plate, where acid in the presoak treatment apparently did not penetrate. (95-micron squares; original magnification 250X.)

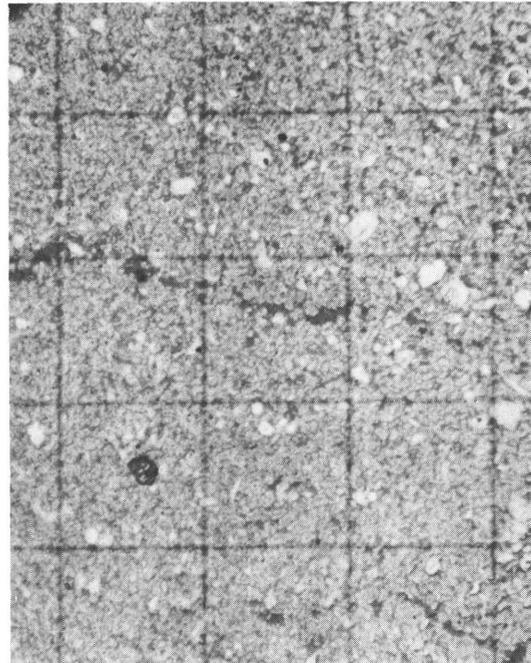
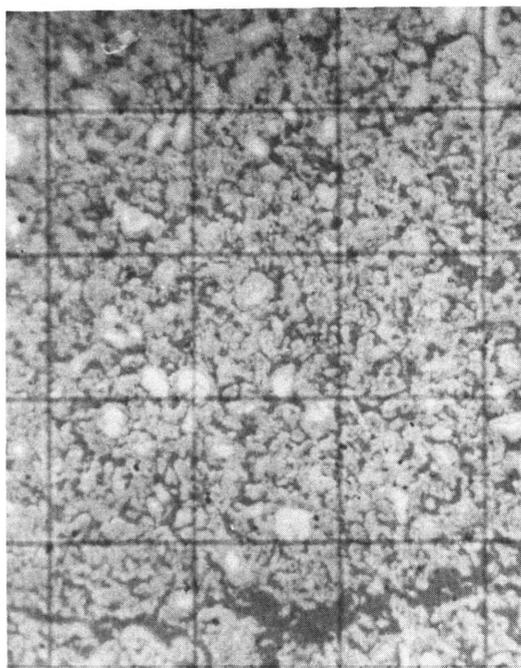


Fig. 24 - Formed area from the plate of manufacturer 1 viewed near the surface, where the presoak presumably penetrated. Note the lower magnification of Figs. 23 and 24 from preceding figures. (95-micron squares; original magnification 250X.)

Fig. 25 - Same area as Fig. 24 but at higher magnification. Note that this is formed material yet still seems to consist of individual particles. Note also that in general there are very few areas of high reflectivity. (30-micron squares; original magnification 800X.)



Oddly enough samples submitted by manufacturer 3 appear to show just the opposite. One plate was formed without any presoak, with the resultant microstructure shown in Fig. 26; the other was formed after a 24-hour presoak in 1.350-sp.-gr. acid, with the resultant structure shown in Fig. 27. While the structure of Fig. 27 appears to be somewhat more porous and to have larger particles than that of Fig. 26, there is no such gross structural difference as appears in Figs. 23 and 24. With these two apparently conflicting pieces of information it may be more logical to look elsewhere for the source of the non-uniform structure found in sample 1.

It is also of interest to report a peculiar phenomenon that appeared in the samples of manufacturer 3. When examined at low magnification the cross section of the oxide appeared to be divided into very distinct regions, each with different reflectivity, microstructure, and distinct boundaries (Fig. 28). The appearance in fact strongly suggested the grain structure found in as-cast, slowly cooled lead. At higher magnification the distinctly different but uniform structure can be seen at each side of the boundary (Fig. 29). At this magnification the boundary itself appears as a continuous barrier between the two portions, and it can be seen that it is not the result of cracking. At still higher magnification (Fig. 27), however, it can be seen that the boundary is not continuous but does appear to be different from the surrounding material.

The reason for this division into definite regions was not evident from the limited number of samples available. It might be the result of nonuniformity of mixing, unequal penetration of electrolyte, or unequal drying, if indeed these were dried before forming.

The structure found in the plates of manufacturer 2 was uniform throughout, although the active material had developed a few cracks during formation. The structure found in this plate was of particular interest because it appears to be a true reticulate or cellular structure such as had previously been found to signify good paste retention in pasted plates when used for float-type service. Its value appears to be that while it presents an open and porous structure, it is at the same time continuous and contains a grid of well bonded material running through it. The nature of this network is shown in Fig. 30.

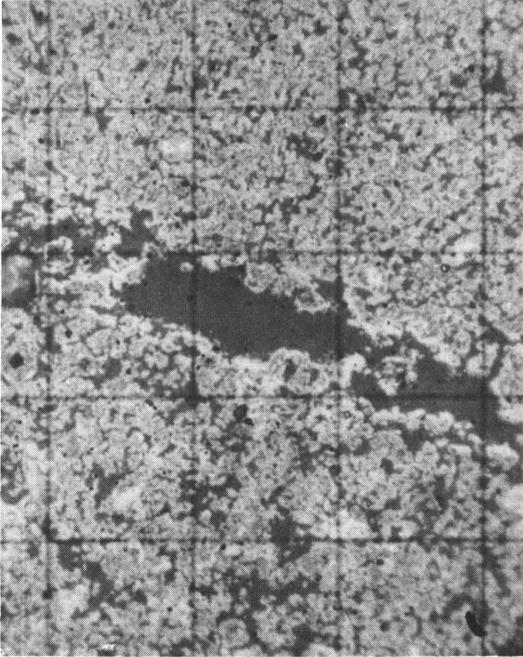


Fig. 26 - Appearance of active material from manufacturer 3 which was formed without a presoak. (30-micron squares; original magnification 800X.)

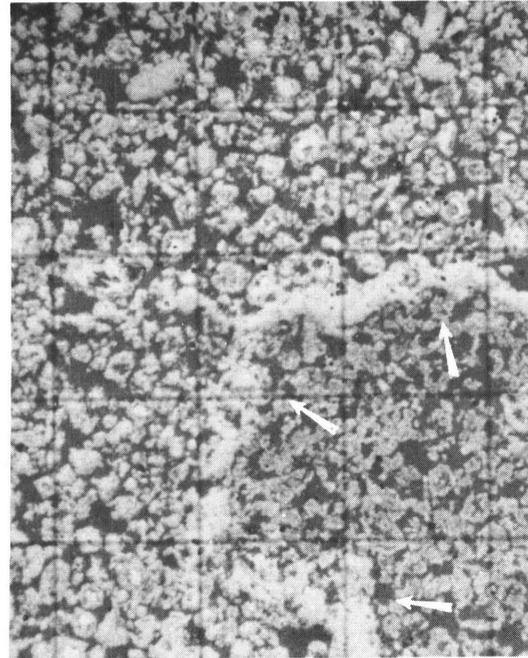


Fig. 27 - Appearance of active material, from the same source as that in Fig. 26 but which was formed after a presoak in acid. The wavy boundary indicated by arrows; and the slightly different structures at each side of the boundary is unexplained. (30-micron squares; original magnification 800X.)

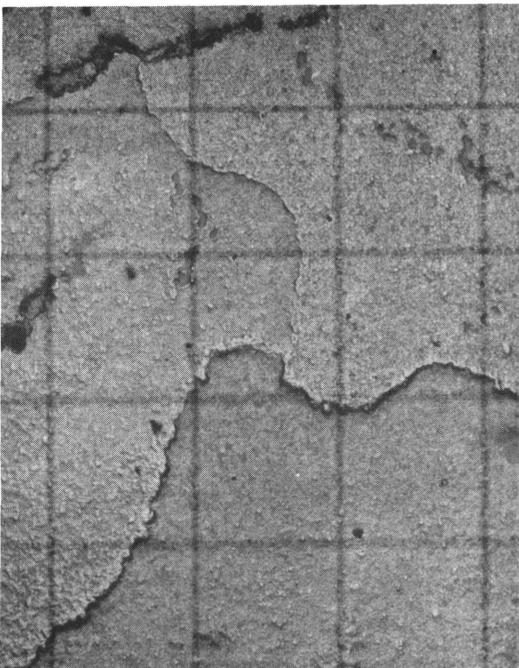


Fig. 28 - Grainlike appearance found in the formed active material from manufacturer 3. Note that the material is slightly different within each boundary, also that the reflectivity is slightly different. (238-micron squares; original magnification 100X.)

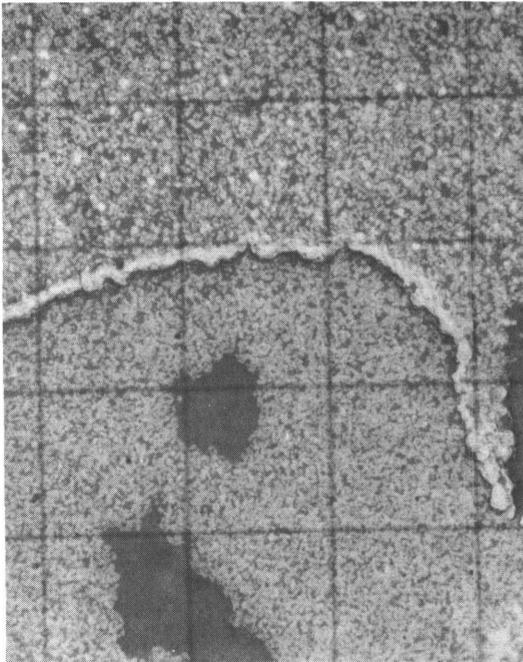


Fig. 29 - A boundary such as seen in Fig. 28 but at higher magnification. Note the distinctly different structure on each side of the boundary also the uniformity of particles in each area. (95-micron squares; original magnification 250X.)

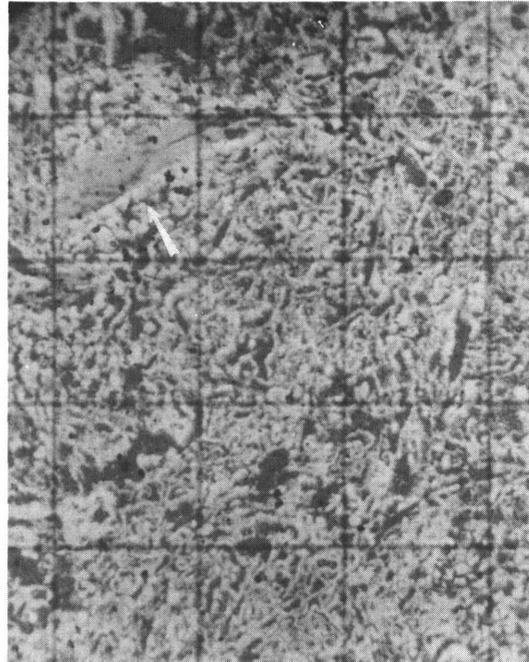


Fig. 30 - Formed material as found in plate of manufacturer 2. Note the definite reticulate pattern of this material, the uniformity, and the lack of individual particles such as seen in Figs. 25 and 27. (30-micron squares; original magnification 800X.)

It will be noted that the distinctive areas present in the unformed as-filled sample have completely disappeared and the same structure now appears in the former areas of either leady oxide or Pb_3O_4 . An exception is presented by those areas formerly occupied by the lead filament at the core of the leady particle. Where these filaments were large, a fairly smooth and nonreticulate area occurs as for example that shown by the arrow.

DISCUSSION

The tubular porous container must be sufficiently tight to retain the fine oxide particles and yet be sufficiently porous so as not to restrict the flow of the electrolyte. The container used by two of the manufacturers appeared to be made up of bundles of glass fibers which were woven into a cloth with a sufficiently tight herringbone weave to leave little or no void space between the individual threads. The material was however very limp and easily damaged by handling. The required rigidity for maintaining a tubular shape so that the container could be fitted around the lead spline and so that it could be easily filled with the oxide was obtained by enclosing the glass cloth in an outer plastic sheath. The latter was pierced by numerous holes so as to impede the flow of electrolyte as little as possible and had evidently been applied while the glass cloth was upon some type of mandrel and with the use of sufficient heat and pressure so that the cloth was imbedded into the plastic and was thus held firmly against the rigid outer sheath. The only visible difference in the product of the two manufacturers using this type of container was that in one the cloth and outer sheath were so firmly bonded together that they could not be separated while in the

other the bond only appeared to have been made at the high points of the weave and the two could be pulled apart without difficulty.

The other type of container was made of some plastic material. Here the container did not consist of separate cylinders applied individually to each spline, as was the case with the other two. Instead the threads had been so woven so that all the containers making up one plate were formed simultaneously, with the threads running completely across the plate and crossing where the individual cylinders met. The resulting fabric is rigid and retains its cylindrical shape with no difficulty, so that no external sheath is necessary. When pulled apart the individual threads are quite stiff and are found to have taken a permanent set in the shape into which they were woven. It is evident therefore that some treatment was applied to these fibers during or after weaving so that they permanently retain the outline of the mandrels over which they were formed. It was thought at first that this might be the result of a coating of some sort, but further examination definitely excluded this and indicated a thermal process.

The material also differed from the others in that it possessed a much more open weave with small square meshes. While not retaining the oxide particles as well as the other two, it appeared to offer less resistance to passage of the electrolyte. However the threads making up both materials were composed of fibers that themselves were not packed too closely together, so that comparison of visible mesh may not indicate true resistance of either material.

Dissection of the individual tubes of the as-filled plate revealed that the material within the tube was a well-caked mass and more so than would be expected from simple packing. Although not mentioned by any of the manufacturers it appears that the tubular plate may have been sprayed with or immersed in water immediately after filling so that sufficient wetting occurred to prevent dusting and sifting out of the oxide particles during subsequent assembly.

No good test was available to judge the relative hardness of the various cylindrical active material sections after forming had taken place, but it appeared that the active material of manufacturers 2 and 3 was much better bonded together than that of manufacturer 1. There did not seem to be any noticeable difference in this respect between 2 and 3; both showed as good and in some cases better cohesion than many pasted and formed grid type plates that have been examined. Formed active material from manufacturer 3 appeared to have about equal hardness and cohesion whether or not the plates were given a presoak in acid before forming. It was noted however that those not given the presoak had a layer of sulfate next to the metal spline which was very evident both on the spline and its counterpart of broken off active material. This sulfate was also visible in the microsection.

From the foregoing it would appear that satisfactory active material can be formed from the lower oxides directly simply by forming in an acid electrolyte. It would appear that a grid-type plate could be formed in a similar way, without the intermediate steps of mixing, pasting and curing, provided a satisfactory temporary support could be used to hold the oxides in place during the forming period. It is inconceivable that such a process has not been tried, and it is concluded that other factors are involved that are not evident from a microscopic examination. One such factor might be that of adherence between the metal of the grid and the active material. Adherence was extremely poor in the case of the tubular positive. It has been noted that the grid metal of pasted but unformed plates has been considerably attacked, apparently by the action of the moist, alkaline paste during the curing period. Such an attack would be avoided in the method of manufacture used in tubular plates yet might be highly desirable to promote adherence between active material and metal.

Examples of pasted and formed plates made from the same oxides or oxide mixes as were used in the tubular plates were not available, but many examples of pasted plates have been examined in both the unformed and formed condition. The structure of the tubular positives resembled none of them, either when the soaked plates were compared with pasted and cured plates or when the formed tubulars were compared with formed pasted plates. The most noticeable difference is in the greater granulation and apparent porosity of the tubular plates and the uniformity of the particle size. The closest approach to matching was between the formed tubular plate of manufacturer 2 and a formed pasted plate which showed a similar reticulate structure; but even these were essentially different.

It had previously been assumed that reticulate structure could appear only in the presence of large crystals of tetrabasic lead sulfate. It is unlikely that tetrabasic lead sulfate would appear under the conditions used in the manufacture of tubular plates, nor were any such crystals detected in the microscopic examination of the material of manufacturer 2; yet a definite reticulate structure is present. Whether this has the same properties as that previously studied cannot be determined without a study of the plates after a period of actual operation.

An examination such as the above which attempts to relate microstructure with performance is of course incomplete without an observation of similar samples from plates that have been in actual operation for considerable periods of time and about which the operational characteristics are known. Hence no conclusions can be drawn as to the relative value of any of the structures observed. It is hoped that these or other manufacturers of tubular plates will offer the author an opportunity to examine such plates not only as filled, after soaking, and after forming but also after various periods of actual use. At the very least they should themselves undertake microscopic examination of their own product to more fully understand its characteristics.

CONCLUSIONS

While the final microstructure of the tubular plates so far examined varied somewhat from that found in other types of plates, no really significant differences were found. Part of the variation may in fact have been caused by the greater proportion of red lead used in the production of tubular plates. Most pasted grid type plates contain no red lead in their formulation, and in those that do the red lead appears to survive unchanged during the mixing and curing, which occur under alkaline conditions.

The primary reason for the use of large amounts of red lead is to increase the ease of formation. Since the tubular type plates encounter rather strong acid during the soaking period, they are essentially converted to lead sulfate. Normal lead sulfate is more difficult to form initially into PbO_2 than are the basic sulfates. The action of sulfuric acid converts a portion of the red lead to lead dioxide; this increases the conductivity of the normal lead sulfate and perhaps even nucleates the formation of additional PbO_2 under the action of the electric current.

Whereas the formation of any of the basic lead sulfates from lead oxide is accompanied by a change of crystalline form, no such change in form accompanies the transformation of red lead to lead dioxide and lead sulfate. All chemical transformations appear to take place within the confines of the original crystal. There is however some change in structure during formation, and this appears to be more pronounced when lead oxide particles are mixed with the red lead.

The structure of the tubular positives is generally more uniform than that found in plates made from paste. This would indicate a fairly uniform reaction throughout the mass and a high degree of porosity.

Structure and cohesion compared favorably with that of pasted plates, which leads to speculation as to the characteristics of flat grid type plates made in a similar manner.

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13. ABSTRACT Tubular type battery plates of various stages of production were obtained from three battery manufacturers and examined microscopically. It was ascertained that certain physical changes took place in the microstructure of the material after soaking in acid and after forming. These changes were not the same as those that occurred when plates were prepared from mixed and cured paste and subsequently formed. To all visible appearances the product from the tubular plate appeared to have cohesion and porosity equal to or better than from most pasted plates. However, the adherence of the paste to the metal spline was poor. Of particular interest was the discovery that the formed active material of one of these manufacturers contained a definite reticulate structure such as had previously been found to coexist with plates that successfully floated without loss of capacity.		

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Batteries and components Storage batteries Anodes Photomicrography Crystal structure Microstructure Lead compounds Oxides Manufacturing methods Electrolysis Sulfuric acid						

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