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NRL Report 5733

AN INVESTIGATION OF ELECTRODE PROCESSES BY MICROSCOPY

PART 2 -THE MICROSTRUCTURE OF LEAD DIOXIDE AND SPONGE LEAD PLATES AS INFLUENCED BY DIFFERENT TEMPERATURES, ELECTROLYTE SPECIFIC GRAVITIES, AND CURRENT DENSITIES IN THE FORMING PROCESS

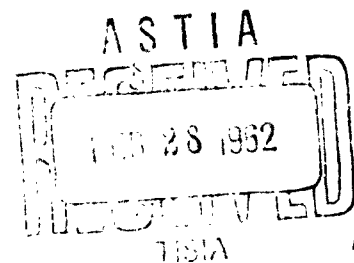
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Electrochemistry Branch
Chemistry Division

February 1, 1962

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U. S. NAVAL RESEARCH LABORATORY
Washington, D.C.

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PREVIOUS REPORT IN THIS SERIES

"Part 1 - Battery Plate Conversion to Lead Dioxide and Sponge Lead From Pastes Made of the Lower Oxides," A. C. Simon and E. L. Jones, NRL Report 5679, October 1961.

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ABSTRACT

In separate experiments battery plates were formed at specific gravities of electrolyte ranging from 1.05 to 1.45, at temperatures from 4° to 80°C, and at current densities from 0.023 to 2.3 amp/dm² (approximately 0.23 to 23 amp/ft²). The time of forming was adjusted in each case so that all samples received the same total current. This total current was 1/4 that required for complete formation of a similar plate under the arbitrarily chosen conditions of 30°C temperature, 0.23 amp/dm² current density, and acid specific gravity of 1.050.

The plates were impregnated with plastic, sectioned, and polished. Microscopic examination revealed wide variation in the total amount of formed material and in its appearance, as well as in the condition of the remaining unformed material.

The area of formed lead dioxide in the positive plate increased as the specific gravity of the acid decreased. Temperatures between 40° and 60°C produced the greatest area of lead dioxide formation at all acid concentrations. The greatest area of lead dioxide formation occurred at a current density of 0.023 amp/dm².

The formed area in the negative plate was found to be greatest at an acid specific gravity of about 1.25. The area of formed material increased as the current density was decreased to 0.23 amp/dm², but no increase was observed at lower current density. The effect of temperature varied with specific gravity of the acid but, in general, best results were obtained between 30° and 60°C.

PROBLEM STATUS

This is an interim report; work is continuing.

AUTHORIZATION

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AN INVESTIGATION OF ELECTRODE PROCESSES BY MICROSCOPY
PART 2 - THE MICROSTRUCTURE OF LEAD DIOXIDE
AND SPONGE LEAD PLATES AS INFLUENCED BY
DIFFERENT TEMPERATURES, ELECTROLYTE SPECIFIC GRAVITIES,
AND CURRENT DENSITIES IN THE FORMING PROCESS

INTRODUCTION

The electrodes of the lead-acid storage battery are manufactured by filling the voids in a lead grid with a paste made by wetting a mixture of lead oxides, consisting chiefly of litharge and red lead, with dilute sulfuric acid. Through the action of the acid this paste is partially converted to lead sulfate and sets up to a hard coherent mass. By subsequent electrolysis these plates are oxidized to lead dioxide when made the positive of the cell and reduced to finely divided metallic lead when made the negative. As a result of this reaction the plates are said to be "formed" and are then ready for assembly into units tailored for definite values of capacity.

The physical change in both the positive and negative plate during this forming process and the basic physical mechanism involved in the conversion to lead dioxide or lead have been made the subject of a microscopic examination and the results have been described in a previous report of this series (1).

Two observations made at that time were instrumental in the instigation of the present work. First, the observation was made that the reduction to lead at the negative plate appeared to operate preferentially at the surface of the plate in intimate contact with electrolyte at the original concentration, while the reaction at the positive plate appeared to occur preferentially in the innermost portion of the plate where the electrolyte concentration would undoubtedly be different because of the problem of diffusion. This seemed to indicate the possibility of an optimum electrolyte forming concentration for one or both plates that might differ from that presently being used in industry and one that might not necessarily be the same for both. Second, it was observed that the use of a higher current density from that commercially employed in the forming process changed the appearance and extent of the formed material even though the same total current had passed through both cells.

It was decided to compare plates that had been subjected to forming at different electrolyte specific gravities, current densities, and temperatures in an effort to detect possible physical changes that would be visible to the eye or structural changes that could be made visible by microscopy. As the subsequent discussion will show, the changing of the forming conditions produced a marked effect on both the structure and appearance in the positive and negative plates.

PROCEDURE

A number of small cells, consisting of one positive and one negative plate separated by a distance of one centimeter, were constructed. Through the kind cooperation of the manufacturer the plates used were already pasted and dried, but unformed, and were of a type used in automotive batteries. The cells were arranged in groups with each group having acid of a different specific gravity, ranging from 1.05 for the lowest group to 1.45

for the highest. One cell from each acid group was then placed in a constant temperature bath and these, when connected in series, were operated at the same current density. This was repeated at current densities of 0.023, 0.23, and 2.3 amp/dm² (approximately 0.23, 2.3, and 23 amp/ft²)*. The water bath was then raised to a higher temperature and the process repeated. Temperatures employed varied from 4° to 80°C. The time that current flowed was so adjusted that regardless of current density each cell received the same total current. This total was chosen as 1/4 the current required for complete formation of a positive plate under the arbitrarily chosen conditions of 30°C, 0.23 amp/dm² current density, and acid specific gravity of 1.050. The reason for using a partially formed plate was twofold. First, a partially formed plate gave a better comparison of the extent to which the various plates were being formed by the same total current, and, second, it was believed that a fully charged plate would yield very little information as to structure. At the time the experiment was begun the technique of relief polishing had not yet been developed and dependence was mainly upon the use of polarized light and the contrast developed between the formed and unformed portions. A fully formed plate would not have this contrast. With the technique of relief polishing, of course, a plate can be examined at any stage. An automatic leveling device added water to maintain the cells at constant level and to replace loss by evaporation. The plates were allowed to stand for 30 minutes at room temperature in their particular electrolyte to insure thorough soaking of the plate before the process of forming began.

As the forming process in each cell was terminated, the plates were immediately disconnected, washed, and dried. They were then impregnated with a catalyzed epoxy resin. After this had hardened, the plates were sectioned in such a manner that a cross section was obtained through the plate and another section was obtained parallel to the face of the plate at about 10 mils below the surface. These sections were then polished (2) and examined with the microscope.

The examination of the specimens revealed so many differences as to make description and correlation extremely difficult. Even examination with the unaided eye revealed startling differences in the amount of apparent forming, in the type of structure produced, and in the color and general appearance of both the formed and unformed portions. Examination at low magnification (2.8 and 13 diameters) revealed differences in the apparent density of the particles in the formed area and in the amount of sulfation that had occurred in the unformed area. High magnification (1000 diameters) revealed a great deal of information about the microstructure and indicated a distinct and progressive change in structure with change in operating conditions.

EXAMINATION OF THE POSITIVE PLATE

The description of the positive plate appearance may be more intelligible if the plates are divided into three groups according to the three different current densities employed.

Plates Formed at 0.023 amp/dm²

These plates, as a group, had the most extensive area covered by the lead dioxide formation. This did not necessarily mean that the greatest amount of lead dioxide was formed in this group but merely that the forming reaction had spread a greater distance from the grid members. The examination of a large number of sections at various magnifications, however, led to the conclusion that this group also represented the formation of the largest amount of lead dioxide.

*dm = decimeter.

Appearance at Low Magnification - In order to present the overall picture the extent of forming, in terms of the area covered, was expressed as percentage of total area and plotted against the variables of temperature and specific gravity of electrolyte, Fig. 1. Figure 2 shows the actual appearance of some representative samples. The view is at an original magnification of 2.8X and shows the appearance of a pellet of active material, retained between horizontal and vertical grid bars, after the plate had been impregnated with plastic and then ground down approximately 10 mils below the surface and polished. The pairs of parallel lines that form a rectangle are the grid bars. The dark areas of the pellet represent the formation of lead dioxide, while the light areas represent as-yet-unformed paste. The figures at the top of the photograph represent the specific gravity of the electrolyte used and those at the left the temperature at which formation took place. All samples received the same total current. In general, the greatest areas of lead dioxide formation and that of best appearance occurred between the temperatures of 20° and 60°C, with a maximum at about 40°C. Above these temperatures the area of formed material rapidly diminished, and at the highest specific gravity considerable shedding of unformed paste occurred. This is shown by the loss of pellets in Fig. 2(i) and by the complete loss of active material and the bare grid of Fig. 2(l). At a given temperature the greatest area of lead dioxide occurred in the plates where the lowest acid gravity was employed. In those plates formed at the lowest specific gravity and at a temperature of 40°C the reaction had spread through the plate from side to side and across the plate from one grid member to another. The 30° and 60° forming did almost as well, Fig. 2(d) and (g). To the eye, or at low magnification, very little unformed material appeared to remain, but at higher magnification it was revealed that small isolated areas of unformed material were scattered thickly throughout the mass of formed lead dioxide.

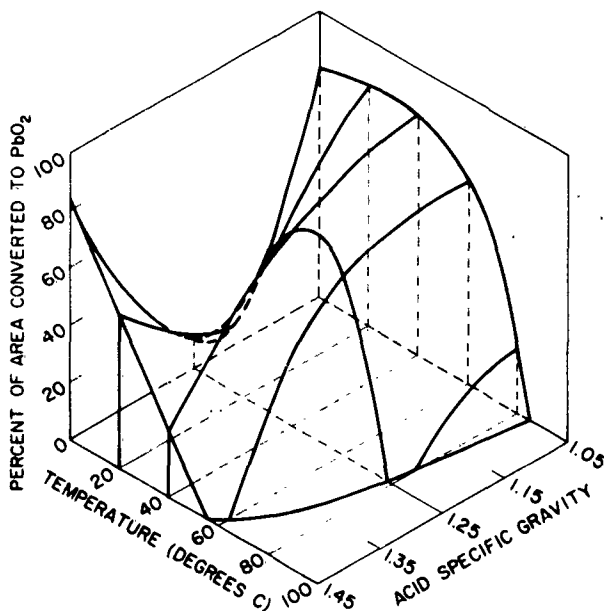


Fig. 1 - The relative area of the positive plate converted to lead dioxide at different temperatures and specific gravities of electrolyte when a current density of 0.023 amp/dm² was used in the forming process. All samples received the same total amount of current. Compare with Figs. 10 and 16 in which the conditions were the same with the exception of the current density value.

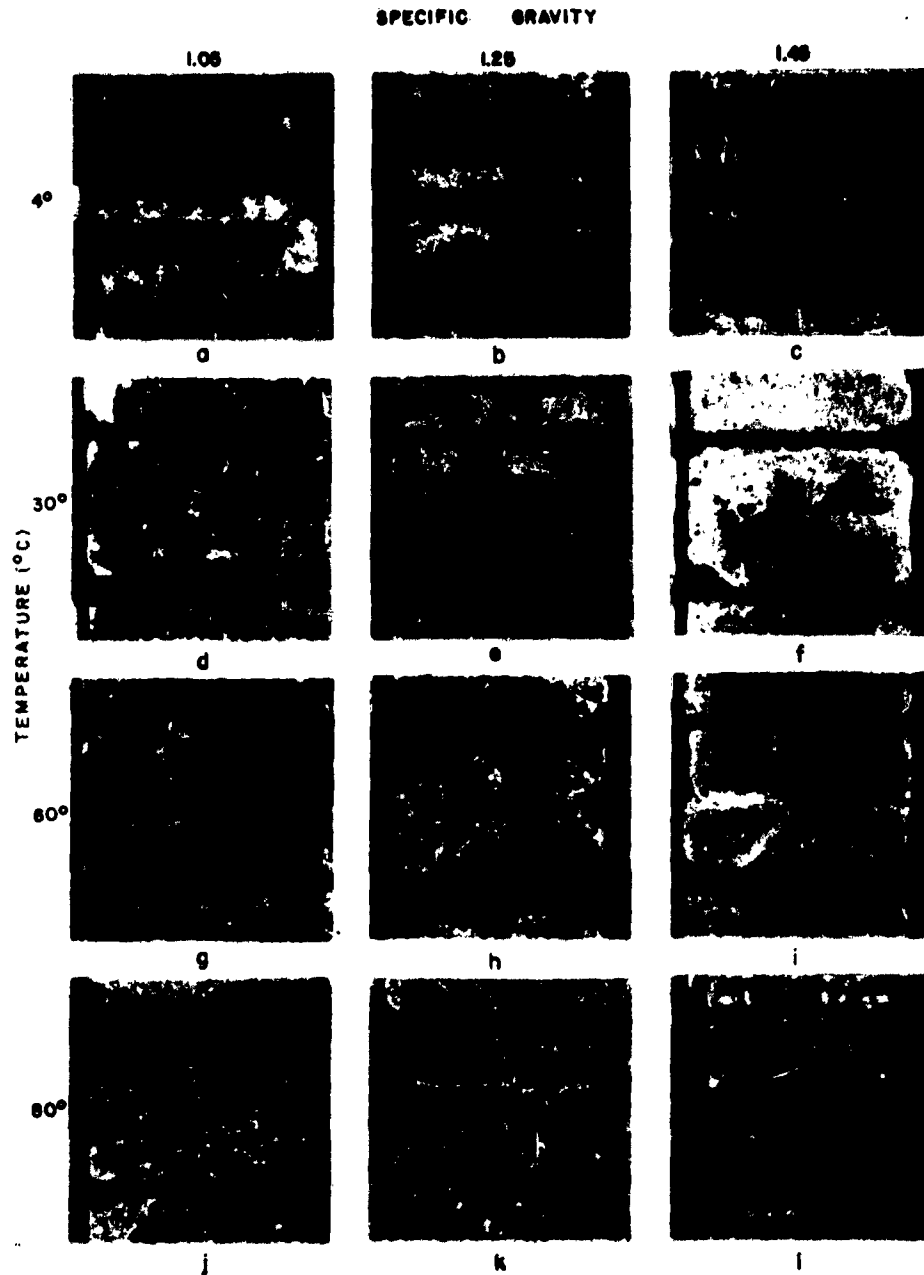


Fig. 2 - Appearance of positive paste formed at a current density of 0.023 amp/dm². Each photograph is of one pellet of active material enclosed between two vertical grid bars that form the sides of the photograph and two horizontal bars that cross the picture near the top and bottom. The unformed paste is light in color, the lead dioxide is very dark. Thus photograph (k) represents an almost completely unformed pellet while photograph (d) represents one in which lead dioxide covers almost the whole area. Photograph (l) represents a grid from which the entire active material has washed out so that the base structure on which the grid rests can be seen through the plastic, as well as an additional horizontal grid bar on the far side of the grid. 2.8X magnification. (Reduction in printing approximately 20%.)

The small patches of lead dioxide in Fig. 2(j) appear to be isolated from one another and from the grid. Continued grinding, however, showed that at greater depths in the specimen there were points at which some of these apparently isolated areas were in contact with the grid and it is assumed that, with sufficient effort contacts could have been found between all of these apparently isolated areas at some level in the sample.

Color of the Plate - The unformed portion of the plate had in all cases faded appreciably from the salmon red of the original unformed plate as received. There was a great deal of difference in the extent to which this had occurred, however. The lightest plate, the one most nearly white in the unformed areas, was produced by the acid of highest specific gravity at all temperatures. In the acid of lowest specific gravity, on the other hand, color was only very slightly lighter than that of the unformed plate until temperatures above 60°C were employed. Intermediate specific gravities of electrolyte produced color fading midway between the two extremes, at comparable temperatures. The color change may have considerable significance because it represents the extent of the conversion of the lower oxides to lead sulfate, which is preliminary to the actual forming of lead dioxide.

Despite the general good coloring in the unformed areas of the plates formed at low specific gravity, it was found under low magnification that a rather pronounced sulfated layer occurred between the grid and the formed area, and at low magnification it appeared as if formation had not begun at the grid surface but at some distance from it, Fig. 3. This layer was quite distinct at the lowest temperature employed but diminished and disappeared as the temperature was raised or the specific gravity increased.

Most of the structure in the plates was revealed by using the technique of relief polishing. By this means softer constituents are preferentially removed and those that are harder stand in relief. This technique revealed no structure in the sulfate layer referred to in the previous paragraph, however. By the use of polarized light a careful search through the layer determined that it was permeated with long needlelike crystals of lead dioxide, Fig. 4, that were apparently too thin to be revealed by the rather coarse definition produced by relief polishing. The presence of these crystals explains how the necessary conductivity was achieved so that the process could be extended beyond the sulfate layer but does not explain why this layer should be formed.

Examination at High Magnification - The usual methods of examination that had previously been employed on these polished specimens revealed little difference in structure, principally because individual details were masked by the density of the formed mass. It was then found that considerable difference in hardness was present among the different crystals that made up the mass, and that this could be exploited to yield a good picture of the crystal forms present if the method of relief polishing was resorted to. The samples were consequently given this treatment and examined at 1000X magnification.

The following generalities can be made concerning this examination. It was found that there was a considerable difference in the hardness of lead dioxide which was dependent upon the method of forming. At low temperature and low electrolyte specific gravity the area of converted material was very large and the lead dioxide so formed was almost black in color. But the lead dioxide was so soft that it could not be differentiated from the background of lead sulfate crystals. In this case it was necessary to resort to polarized light and reveal the structure through the difference of color of the formed lead dioxide (red) and the background of lead sulfate crystals (white), Fig. 5. The long needlelike crystals of lead dioxide visible in the picture probably explain how the formed area of the plate became so extensive, the long crystals acting as conductors to spread the reaction over a large portion of the plate.

If the temperature was maintained low but the specific gravity of electrolyte was increased, it was found that hard and soft lead dioxide were both formed, Fig. 6. A hard

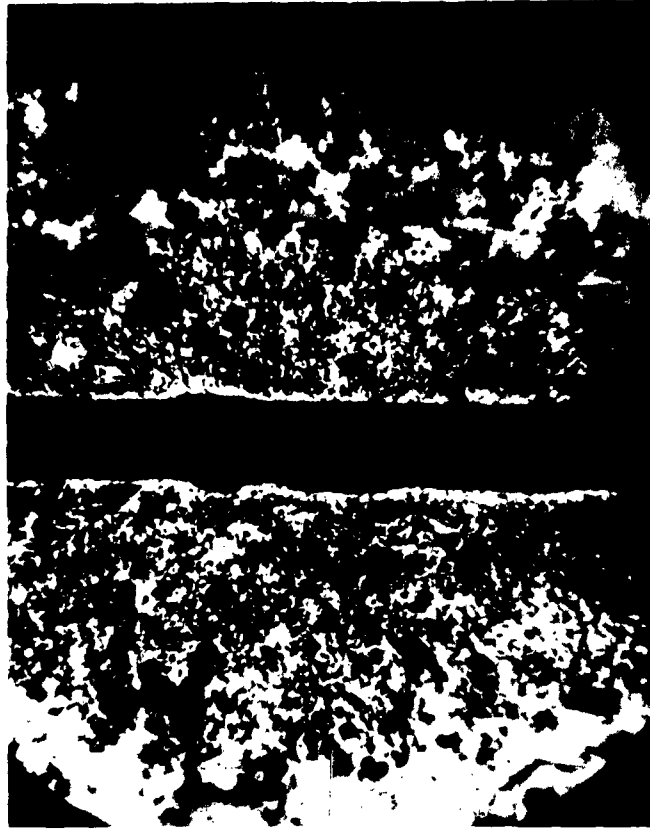


Fig. 3 - The formation of a sulfate layer next to the grid bar of the positive plate. A section parallel to and about 10 mils below the surface of the plate is shown. The plate was formed in 1.05 specific gravity acid at 15°C and with a current density of 0.023 amp/dm². The section of the grid bar crosses the photograph about midway from the top. The thin white line appearing parallel to the bar on either side is the sulfated layer. Beyond this can be seen a rather fibrous appearing mass of dark lead dioxide particles which have appeared as a result of the forming process. 13X magnification.



Fig. 4 - Photomicrograph of the type of long needlelike lead dioxide crystals found in the sulfated layer of the previous photograph. The dark vertically elongated area to the left of the photograph is a portion of the metal grid as it appears under this illumination. The light colored areas of the field of view represent unconverted lead sulfate. Note that the needlelike lead dioxide particles have random orientation with the grid. Illuminated by polarized light. 1000X magnification.



Fig. 5 - Appearance of a partially formed positive plate that is too soft to show structure by relief polishing. A combination of polarized light and a retardation plate has been used to simultaneously show the appearance of the polished surface and the underlying structure that can be differentiated from the background only by color. Conditions of forming were similar to those of Fig. 3, but a temperature of 30° C was used. 1000X magnification.



Fig. 6 - Appearance of sample formed in 1.25 specific gravity acid at 4°C with a current density of 0.023 amp/dm² after relief polishing of the surface. A small portion of the metal grid appears at upper right, the remainder of the picture represents active material. Note rectangular or needlelike areas outlined by hard raised material, which is a harder, more dense form of lead dioxide. 1000X magnification.

outer layer of lead dioxide has evidently been formed on underlying crystals of lead sulfate so that, when sectioned, their form is outlined by the hard lead dioxide standing in relief. The interior of these crystals has been also converted to lead dioxide but of a softer form, as has also the area immediately surrounding the crystals. In view of the previous statement regarding the relationship between the area of formed material and the long needle-like dendritic crystals, it is interesting to note that these crystals are shorter and less needlelike, while at the same time the area converted is much less than in the previous case. The lead dioxide is also lighter in color, tending to be more reddish-brown.

When the temperature was maintained at the same low level but the specific gravity of electrolyte was increased to 1.45, the maximum of the series, it was found that the lead dioxide again became soft and no structure was visible under relief polishing. Polarized light revealed a formless mass of lead dioxide of about the same color and extent as in the case just discussed, though careful examination revealed no needlelike crystals or, in fact, any recognizable structure in the formed areas, Fig. 7.

As the temperature was increased for a given specific gravity there was a tendency for a coarse granular type of hard particle to appear, without definite shape and uniformly hard throughout, Fig. 8, while the other type of structure, the rectangular or needlelike crystals, were completely absent.

Corrosion of the Grid - While not directly related to the present problem, the problem of grid corrosion was also apparent. The same reaction that produces lead dioxide in the paste of the plate also converts the outer lead of the grid into lead dioxide. It was interesting to note that the amount and type of this corrosion varied with the conditions of forming. Since these samples were all formed at the same low current density, they were all necessarily in the electrolyte for a total of 80 hours, sufficient for some corrosion to take place. There did not seem to be much relationship between the type of corrosion and the lead dioxide structure found in the plate, but the following is of interest. Figure 5 shows a specimen formed at low temperature and low specific gravity of electrolyte which exhibits a very definite, thin, hard layer of corrosion product with well-defined outline. Figure 7 shows something quite different. It is usual for a well-defined chain of antimony particles to outline the surface layer of such a lead-antimony alloy due to inverse segregation. Such a chain is visible near the edge of the grid section shown. However, the usual anodic corrosion process begins with the removal of all antimony at the surface of the grid and continues with the antimony being removed preferentially to the lead wherever it is exposed to the electrolyte. It is evident that under conditions of low temperature and high specific gravity of electrolyte that this process is reversed and the lead is preferentially attacked so that the antimony is left apparently completely unattacked. It should also be noted in this connection that corrosion into the lead is proceeding without the formation of the hard, dense, apparently protective layer of lead dioxide, such as is usually observed and was shown in Fig. 5. It is also interesting to compare these two photomicrographs with Fig. 9, which shows a specimen formed at the same low specific gravity as was the sample shown in Fig. 5 but at the high temperature of 80°C. It will be seen in Fig. 9 that the corrosion layer is quite thick, that the attack is not uniform, and the the layer does not show any antimony particles in it. It is also interesting to note the quite large sulfate crystals that appear in the unformed paste under these conditions. The area of formed material is quite small and irregularly distributed along the grid bars so that at some points formation appeared to be somewhat extensive and at others, as here, there was no formation at all.

Plates Formed at 0.23 amp/dm²

Appearance at Low Magnification - The area of formed material was not nearly as large in this group as in that formed at the lower current density. Figure 10 shows the relative areas covered by the formed material under various conditions. Again the maximum appeared to be at the lowest specific gravity of electrolyte and over a temperature

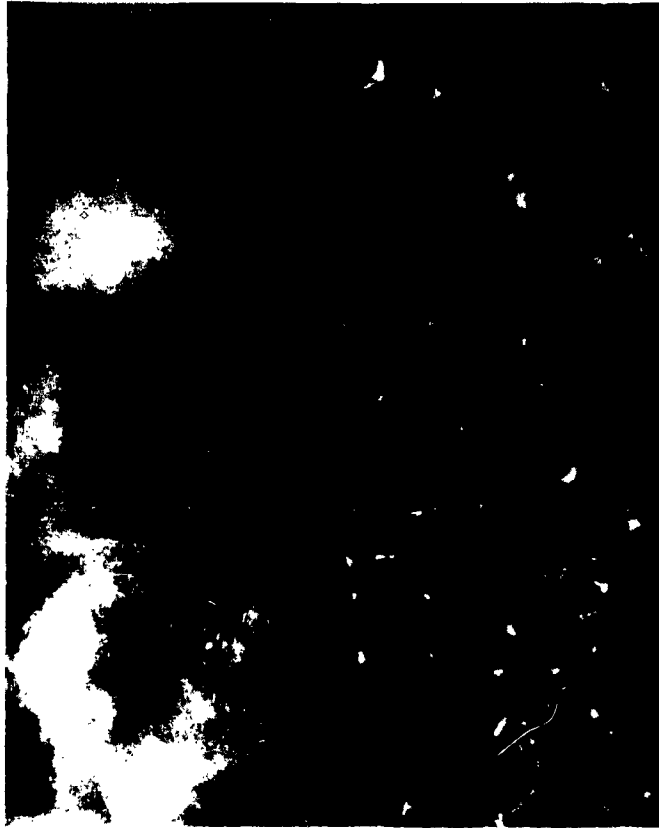


Fig. 7 - Appearance of positive plate when the specific gravity was increased to 1.45, the temperature of 4°C and the current density of 0.023 amp/dm^2 being the same as in Fig. 6. The lead dioxide was too soft to reveal structure by relief polishing, so polarized light was used. The dark vertically aligned area on the right half of the picture is a portion of the metal of the grid. The light particles in this area are segregated antimony since the grid is a Pb-Sb alloy. Approximately bisecting the picture from top to bottom is a line of antimony particles that represent the original metal surface, viewed here in cross section. Note that corrosion has proceeded into the metal beyond this point without attacking the antimony and that the corrosion-metal interface is very irregular and free of a layer of corrosion product. Also note absence of structure in the left half of the picture which represents the condition of the active material. 1000X magnification.



Fig. 8 - An example of the hard, coarse, irregular structure developed at higher temperature for a given specific gravity and current density. This plate was formed at a specific gravity of 1.25, a temperature of 60°C, and a current density of 0.023 amp/dm². Compare with Fig. 6. A portion of the metal grid appears at the left, the outer boundary has an almost continuous layer of corrosion product, which is also a hard form of lead dioxide. 1000X magnification.

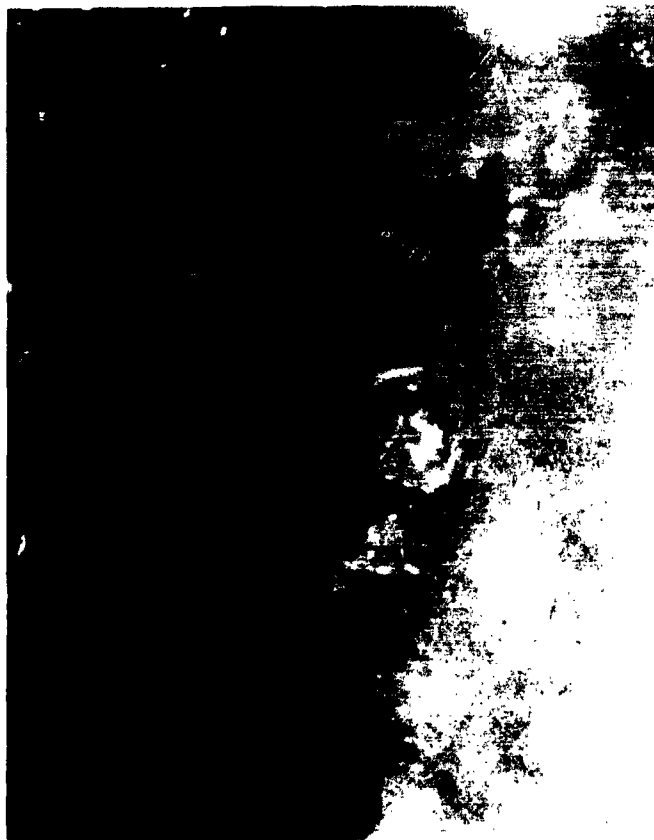


Fig. 9 - This photograph demonstrates the increased corrosion that accompanied forming at high temperature. This positive plate was formed at the same current density and specific gravity as was that in Fig. 5 but at the higher temperature of 80°C. The metal grid appears at the left, the corrosion layer at the left center, and the unformed paste, consisting now almost entirely of sulfate crystals, is at the right. 1000X magnification.

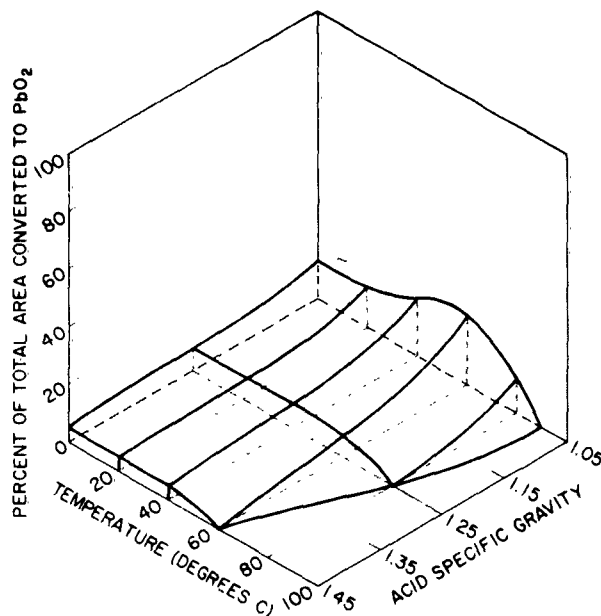


Fig. 10 - The relative area of the positive plate converted to lead dioxide at different temperatures and specific gravities of electrolyte when a current density of 0.23 amp/dm^2 was used in the forming process. All samples received the same total amount of current as did those of Figs. 1 and 16.

range of between 40° and 60°C . Figure 11 shows the appearance of some of the specimens. These illustrations show the most common condition of the plate in each case, because with increasingly high current densities the plates showed a greater tendency for nonuniform reaction. Some pellets of the plate would form almost completely, while others would remain almost completely unreacted. This seemed to be related to the condition of the contact of the pellet with the grid bars since some of the pellets were found to be very loosely attached in the dry, unformed plate, and microscopical examination always showed large areas of no contact in those pellets that were the least reacted. It will be noted that a formed area is present in the center of many of the pellets, as for example in Fig. 11(g). This is directly over an unseen grid bar. The horizontal grid bars are usually staggered so that the paste is more firmly retained. The two bars visible are on the near side of the plate, while another is positioned parallel and midway between them on the far side.

Comparison of the group of photographs in Fig. 2 with those of Fig. 11 shows the much greater area covered by lead dioxide in the former, under the condition of lower current density. On the other hand, it should be noted that where formation of lead dioxide has occurred in Fig. 11, under conditions of higher current density, the areas so formed appear much more completely converted and are darker in color. This indicates that the total weight of lead dioxide formed in the two cases may not differ as much as appears at first glance.

Reference to Fig. 11(i) and (l) will also show that the paste of those plates electrolyzed at high specific gravity and temperature, while very little converted to lead dioxide by the treatment, is still much less damaged than that subjected to a lower current density for a longer period (Fig. 2(i) and (l)).

Color of the Plate - The color of the formed material appeared to be a very uniform dark chocolate brown. The unformed paste was considerably lighter in color than the original as-received material, and although the total time in the electrolyte was only 8 hours, as against 80 hours for the lower current density group, the darkest yellow in this group was not as dark as the darkest of the previous group. The lightest paste, most nearly white, occurred at the lowest specific gravity and temperature; those formed at other

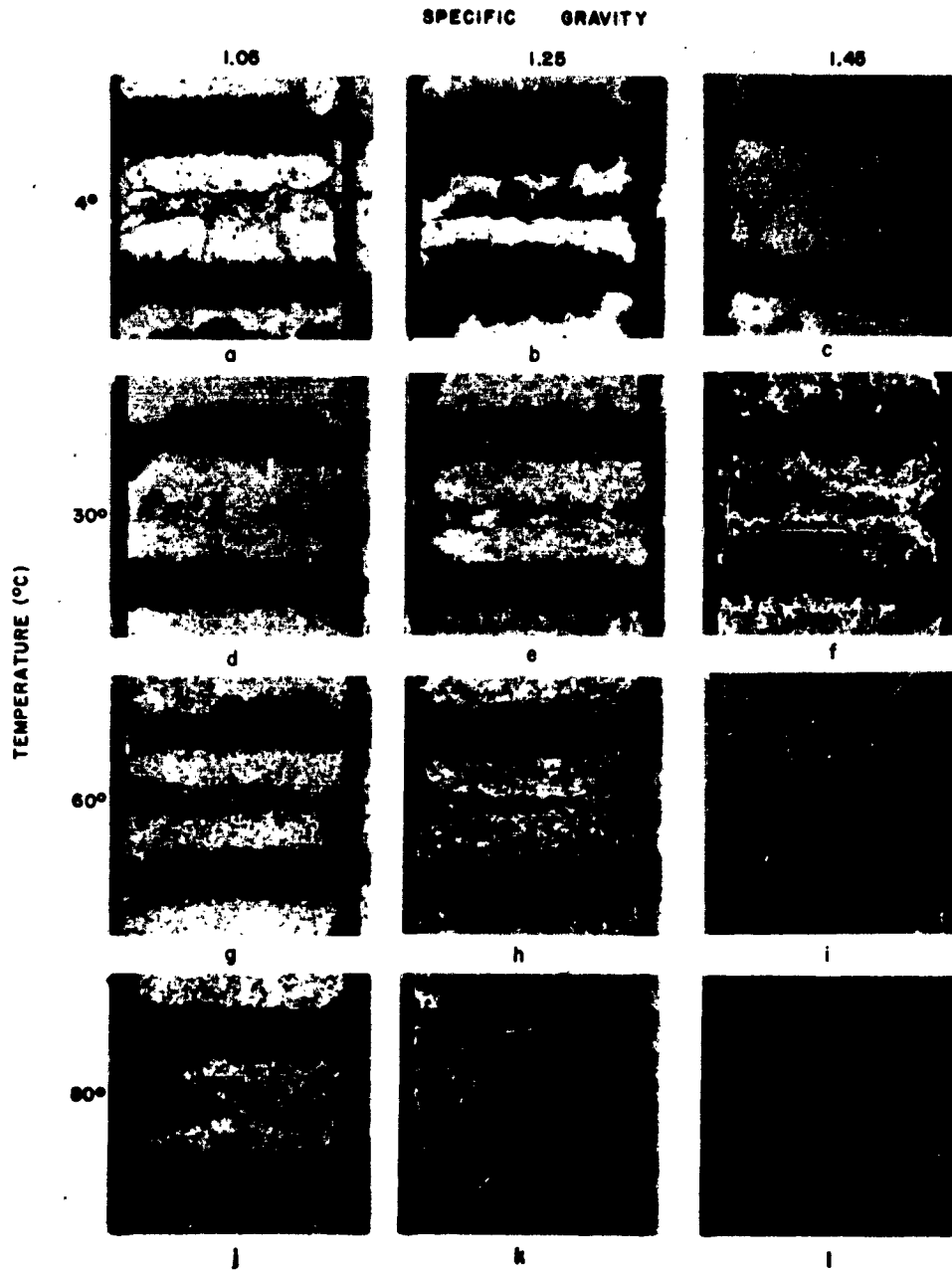


Fig. 11 - Appearance of plates formed at a current density of 0.23 amp/dm² and at the specific gravities of electrolyte noted at the top and the temperatures noted at the left side of the figure. Compare these photographs with those of Fig. 2 to note the greatly reduced area covered at this current density. 2.8X magnification. (Reduction in printing approximately 20%.)

specific gravities and at the lowest temperature were also very light in color but with a much more yellow tinge than that just described. The remaining plates were between these extremes but did not vary much in color among themselves.

Examination at High Magnification - At the lowest temperature and specific gravity of this group the plate showed both soft and hard material, and the latter appeared as long needlelike particles, Fig. 12. But these needles were not nearly as large as those found under the same conditions for the group of lower current density. Maintaining the temperature constant and increasing the specific gravity produced a change in structure to that shown in Fig. 13 which strongly resembles the type obtained with similar conditions of temperature and specific gravity of electrolyte but a lower current density, Fig. 6.



Fig. 12 - The type of needlelike crystals formed in the positive active material at a current density of 0.23 amp/dm^2 when the specific gravity was 1.05 and the temperature 4°C . Note that these crystals show a vestige of soft centers like those in Fig. 6. 1000X magnification.



Fig. 13 - Example of the structure produced when the sample was formed at a current density of 0.23 amp/dm^2 and a temperature of 4°C . Increasing the specific gravity to 1.25 has produced a change from the structure noted in Fig. 12. Compare also with Fig. 6. 1000X magnification.

As in the previous series the highest value of specific gravity produced a return to the soft structureless form quite similar to that shown in Fig. 7. Also, as in the previous case, an increase in temperature within any specific acid group tended to coarsen the structure until it eventually appeared as in Fig. 14. It is worthwhile to note that the softer material with which these hard coarse particles are surrounded is much darker than that formed under other conditions, and that these irregular or formless crystals, when examined by polarized light and careful traverse of a suitable depth of the section by means of the fine focus adjustment, are found to be quite regular crystals of the form shown in Fig. 15. The crystals shown in this figure are of course sulfate crystals and, as such, are sufficiently transparent so that their form can be shown and photographed by polarized light that penetrates the polished cut surface and is reflected back from the inner side of the crystal faces that are present below the plane of the section. The crystals under discussion are quite opaque and cannot be photographed in the manner of the sulfate crystal. Their sections, taken at odd angles through the crystals, produce the irregular shaped particles seen in the photograph.



Fig. 14 - Coarse structure obtained by increasing the temperature. The conditions are otherwise like those of Fig. 13, but temperature of forming has been increased to 80°C. 1000X magnification.

Corrosion - In this case, as with the lower current density group, the lead was attacked in preference to the antimony at low temperature and high specific gravity of electrolyte, and no dense protective film of lead dioxide was formed. Likewise, the thickest hard-and-dense lead dioxide corrosion product was formed at the highest temperature and lowest specific gravity of electrolyte. The general behavior of the paste, in the case of low temperature and high specific gravity, seemed to agree with the result obtained in corrosion. That is, there was little or no lead dioxide formed. The other condition, however, of high temperature and low specific gravity, which led to a heavy corrosion film of lead dioxide, did not produce a corresponding high yield of lead dioxide in the paste.



Fig. 15 - Large lead sulfate crystals found in unformed areas of plate treated as in Fig. 14. Examination with polarized light in areas of formed material disclosed crystals identical in size and shape with those shown here but black and opaque, indicating a direct transformation from lead sulfate to lead dioxide. 1000X magnification.

Plates Formed at 2.3 amp/dm²

Appearance at Low Magnification - These plates showed very little area of formed material. The forming that had occurred was confined to a region very close to the grid members and was somewhat irregular in its outer boundaries and did not form uniformly along the entire grid. The formed lead dioxide appeared to be very hard and dense, and within the area where forming had taken place very little unformed material could be found. Figure 16 expresses graphically the extent to which formation occurred, and Fig. 17 shows the appearance of some of the plates. As in the previous cases the best results were obtained at low specific gravity of electrolyte and fairly low temperature.

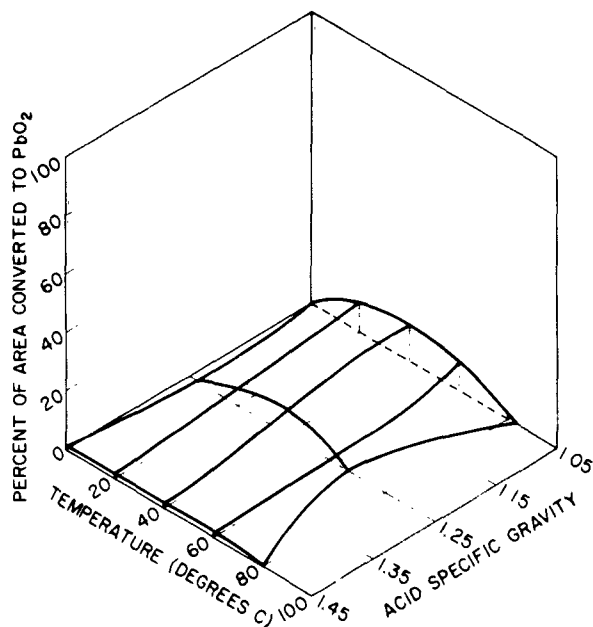


Fig. 16 - The relative area of the positive plate converted to lead dioxide at different temperatures and specific gravities of electrolyte when a current density of 2.3 amp/dm^2 was used. All samples received the same total current.

Color of the Plate - As mentioned above, the formed oxide was dark in color and appeared very dense, while the unformed material was a very light yellow. On the average these specimens were very light, yet all retained the yellow color. This was not always true in the previous conditions of lower current densities where several samples in each group were almost pure white in the areas where formation had not taken place.

Appearance Under High Magnification - Low temperature and low specific gravity produced a uniform structure that was hard and dense but showed no dendritic or needle-like crystals. Instead, it appeared to be made up of very small irregular-shaped particles, Fig. 18. As can be seen from Fig. 16, there was very little area covered by this material.

At the same low temperature, increasing the specific gravity at first produced some evidence of needlelike structure, but this was not present in any great amount. As in the previous cases very high specific gravity caused a return to a soft, formless lead dioxide.

For a given specific gravity, increasing the temperature produced a decided tendency for the structure to become coarser, but this did not continue to the point where the particles were very coarse and of irregular shape, such as in Figs. 8 and 14, but only to the point where rectangular crystals were made visible by a coating of lead dioxide, Fig. 19.

Corrosion - The same characteristics as previously mentioned were also present at this current density. Although these samples were subjected to the electric current for only 48 minutes, at low temperature and high specific gravity of the acid there was produced the same preferential attack on the lead as mentioned previously and to just about the same extent. At the same time the antimony remained unattacked. The thickest lead dioxide corrosion product was likewise produced at the highest temperature and lowest specific gravity of the electrolyte.

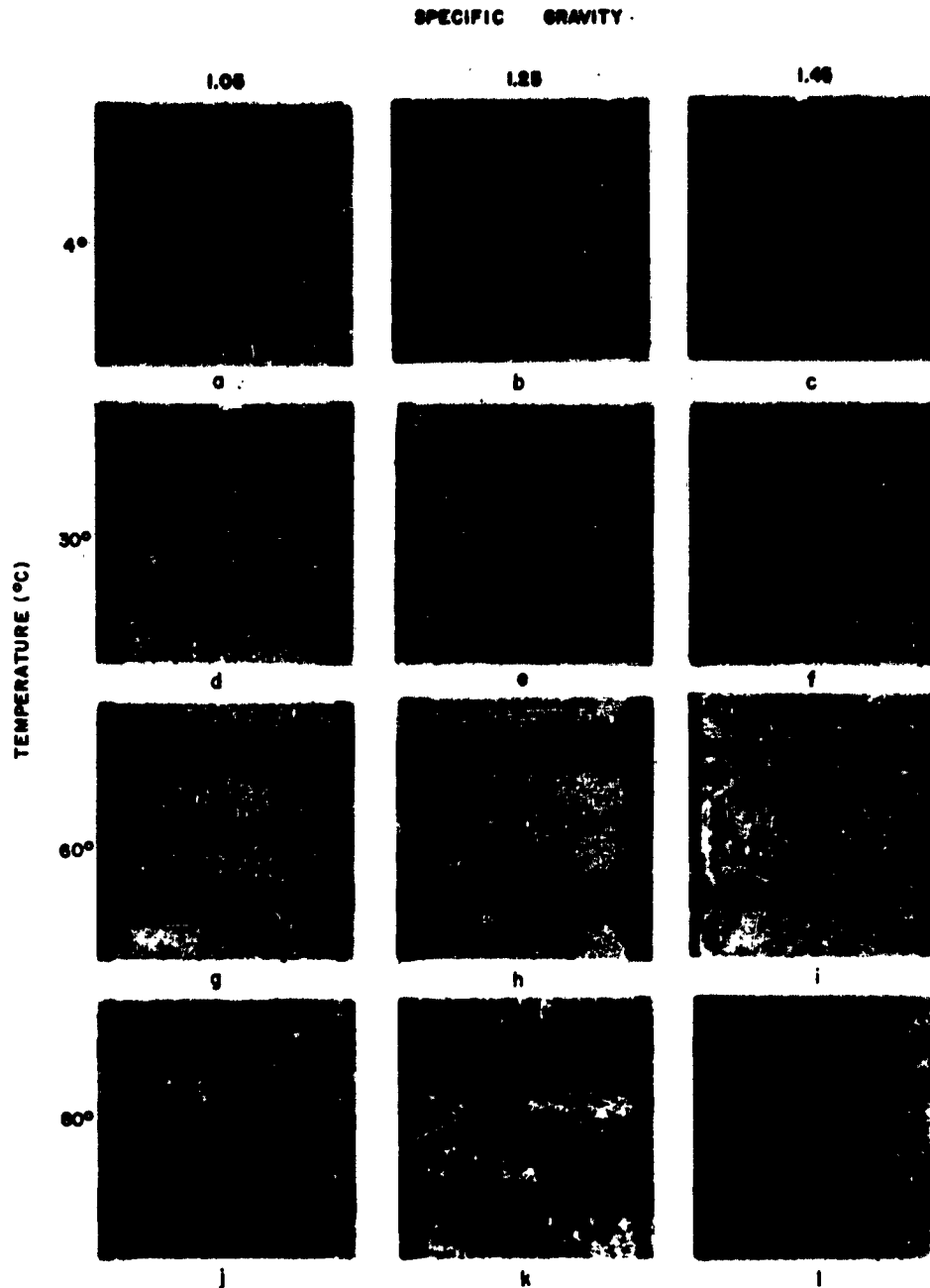


Fig. 17 - Appearance of plates formed at a current density of 2.3 amp/dm² and at the specific gravities of electrolyte and temperatures designated on the figure. Compare with Fig. 2 and Fig. 11 to see how increasing the current density decreases the area of lead dioxide although the total current flow was the same in all cases. 2.8X magnification. (Reduction in printing approximately 20%.)



Fig. 18 - The appearance of an area of lead dioxide formed at 2.3 amp/dm^2 in acid of 1.05 specific gravity and at 4°C . A portion of the grid section occupies the left side of the picture while the active material, seen at the right, has a dense and hard surface divided into many very small hard particles. 1000X magnification.



Fig. 19 - Appearance of lead dioxide formed as in the specimen shown in Fig. 18 except that the temperature was increased to 80°C. Note that the outlined particles still have soft centers, unlike the examples given at high temperature but lower current density, as for example Figs. 8 and 14. 1000X magnification.

Summary

For a given total current the greatest area of conversion to lead dioxide took place at the lowest current density (0.023 amp/dm^2), at a temperature of approximately 40°C , and with an electrolyte specific gravity of 1.050. Under these conditions there were found in the formed area long, needlelike crystals of lead dioxide which appeared to be much harder than the background material which consisted of lead dioxide crystals of small, roughly spherical shape that appeared to be a softer form of the oxide. The area of the plate material which formed decreased at both high and low temperatures. The maximum area of formed material appeared to be coincidental with the presence of the long, needlelike crystals. As the temperature was increased these crystals tended to become larger and more irregular in general outline, and the area of formed material decreased. As the specific gravity was increased the hardness of the lead dioxide became greater and the crystals that formed were shorter and more rectangular in appearance, but this was also accompanied by a reduction in the area of formation. At the highest specific gravity, the crystal structure, hardness, and area of formed material appeared to reach a minimum. As the current density was increased the structure appeared to become finer, the lead dioxide became harder, and the particles became more uniform in shape, but this was also accompanied by a decreasing area of formed material.

EXAMINATION OF THE NEGATIVE PLATE

In the case of the negative plate the effect of varying the forming conditions was not as marked as in the case of the positive, although there was a definite effect. The description of what occurred under the varying conditions can therefore be made somewhat less involved than for the positive. The same convention of separation into groups of the same current density will be used.

Plates Formed at 0.023 amp/dm^2

Appearance at Low Magnification - The area of formed material was quite large. As seen by reference to Fig. 20 there was a definite maximum for the area of formed material when operating at a specific gravity of approximately 1.25 and at a temperature of about 40°C . While a decided drop toward zero is shown in the envelope at the highest specific gravities and temperatures, the actual condition is not known with certainty because there was a decided loss of active material at all temperatures when high specific gravities were used and this became catastrophic above room temperature. Where any active material remained, the material had been formed. Figure 21(f), (i), and (l) illustrate this point. In the case of the negative plate, the grid bars are spaced slightly closer than in the positive so that two pellets are included in the field of view for each plate. The magnification is the same as previously used, 2.8X. The extent to which the bars on the other side of the plate are visible will assist in judging how much active material has been lost from the plates run at high specific gravity, Fig. 21(c), (f), (i), and (l).

As would be expected, the negative was more damaged than the positive under the same conditions since this plate was thinner than the positive, and the paste was broken up and separated by numerous cracks even when dry and would thus be more easily dislodged than would the solid mass of the positive.

The light areas in the pellets indicate unformed material while the dark areas of approximately the same shade as the grid bars represent conversion to metallic lead crystals. The cracks outlined in white at the higher temperatures represent high concentrations of lead sulfate crystals (that have formed from solution) within the cracks rather than representing unformed areas of the original paste.

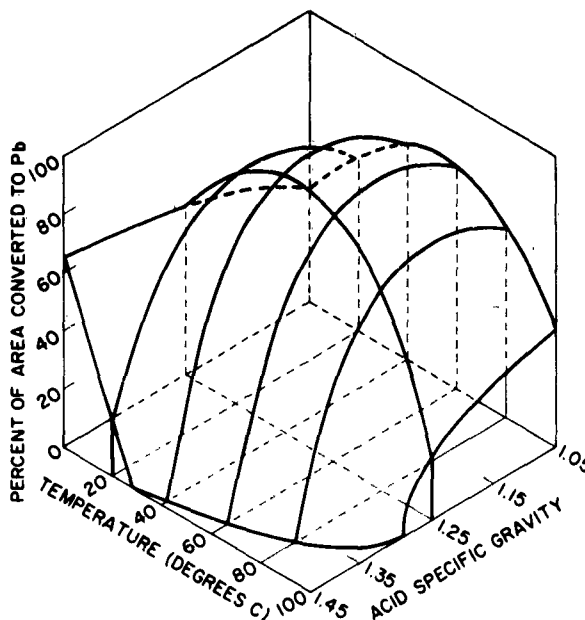


Fig. 20 - The relative area of the negative plate converted to lead at different temperatures and specific gravities of electrolyte when a current density of 0.023 amp/dm² was used

Color of the Plates - The plates were a uniform slate gray where formation had taken place. In the case of the remaining unformed material a peculiar condition existed. In the experiment investigating the actual process of formation (1), it was noticed that in the immediate vicinity of the formed lead there was a change in color of the as-yet-unformed active material of the negative which caused it to darken and lose the yellow color. It was found that this was brought about by an actual change in the lead sulfate crystals. Whereas in the dry plate they appeared rough and frosty white, they were not found to be translucent in large numbers. This caused the unformed portion of the plate in some areas to become as dark as that portion containing actual lead crystals. This made it necessary to check each section at fairly high magnification to see whether the boundaries of the formed area were as they appeared to be.

Appearance at High Magnification - Only two types of structure were observed in the negative plate, and their examination required the use of polarized light since the method of relief polishing used with the positive did not appear to be effective. The lead crystals found were either long, needlelike, dendritic crystals or irregular, roughly spherical particles. The major difference produced by varying the forming conditions was to vary the size of these crystals and to convert one type into the other.

The lowest temperature and lowest specific gravity produced the needlelike crystals with the largest size, although with a somewhat greater girth than was normal, Fig. 22. Increasing the temperature appeared to have but slight effect on crystal size, although the crystals did tend to become smaller and more slender. Increasing the specific gravity produced a marked coarsening of the structure, and the dendrites tended to become quite small and to appear in clumps. At the highest specific gravity these clumps appeared to be replaced by irregular lead particles which conceivably could still consist of clumps of very small needlelike crystals, but, if so, these were below the limit of resolution, Fig. 23.

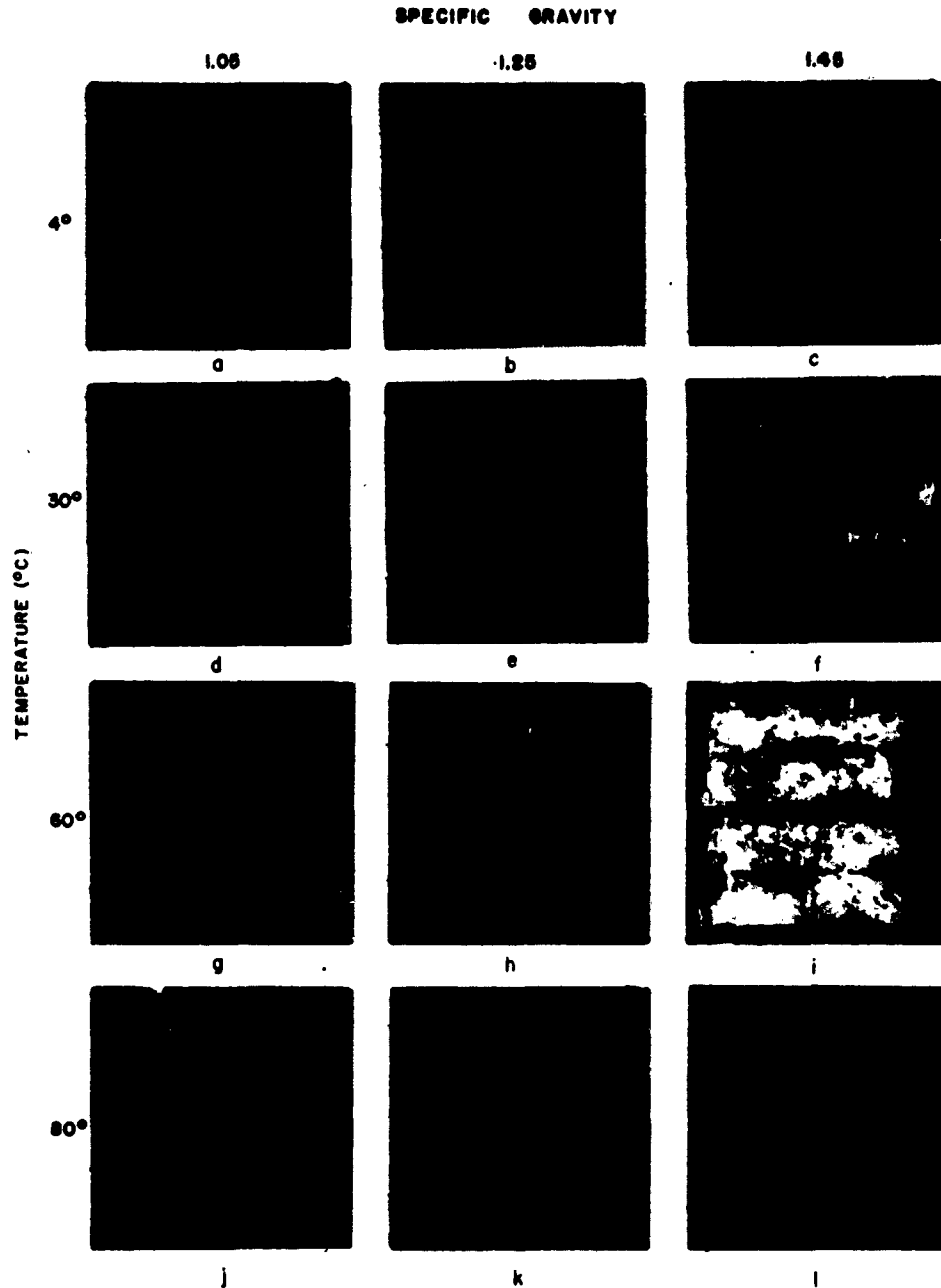


Fig. 21 - Appearance of various negative plates when a current of 0.023 amp/dm² was used. Photographs (f), (i), and (l) show practically bare grids since this active material was largely washed away during the forming attempt. As in the positive the light areas represent unformed paste. Dark areas represent either conversion to lead or to translucent lead sulfate crystals as discussed in the text. 2.8X magnification. (Reduction in printing approximately 20%.)



Fig. 22 - The relatively large needlelike crystals of lead which are formed at a current density of 0.023 amp/dm^2 , an acid specific gravity of 1.05, and a temperature of 4°C . Illumination is by polarized light. The dark particles represent metallic lead and the white areas unconverted lead sulfate. 1000X magnification.



Fig. 23 - Transformation of structure in the negative plate to coarse particles is illustrated when the conditions were as in Fig. 22 except that the specific gravity of electrolyte was increased to 1.45. A tendency for some of the lead sulfate particles in the upper part of the picture to appear somewhat translucent will be noted. 1000X magnification.

Plates Formed at 0.23 amp/dm^2

Appearance at Low Magnification - Figure 24 shows the area formed under the different conditions employed. Comparison of Figs. 20 and 24 shows that a tenfold increase in current density has produced but slight difference in the area of formation. This current density was slightly less destructive to plates in high specific gravity electrolyte since there now appeared to be very little tendency for active material to shed even at high temperature, Fig. 25. Another effect was noted at this current density that had not previously been so pronounced. There was a marked sulfation in the cracks of the plates that were formed in high specific gravity acid. This effect in certain cases was quite pronounced, as can be seen from Fig. 26.

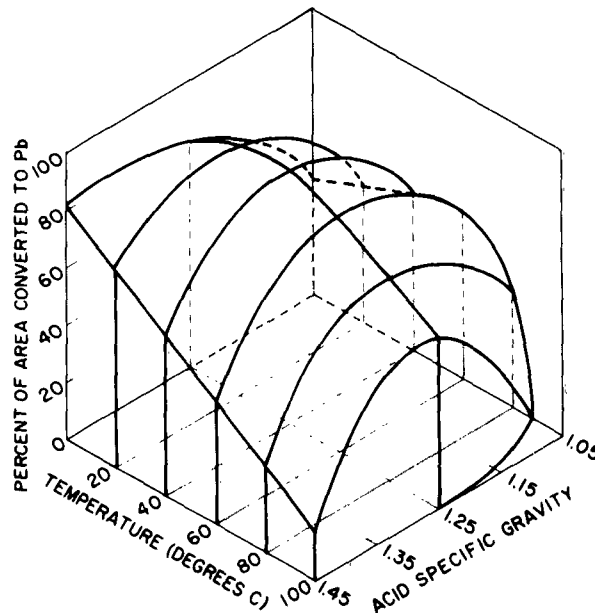


Fig. 24 - The relative area of the negative plate converted to lead at different temperatures and specific gravities of electrolyte when a current density of 0.23 amp/dm^2 was used

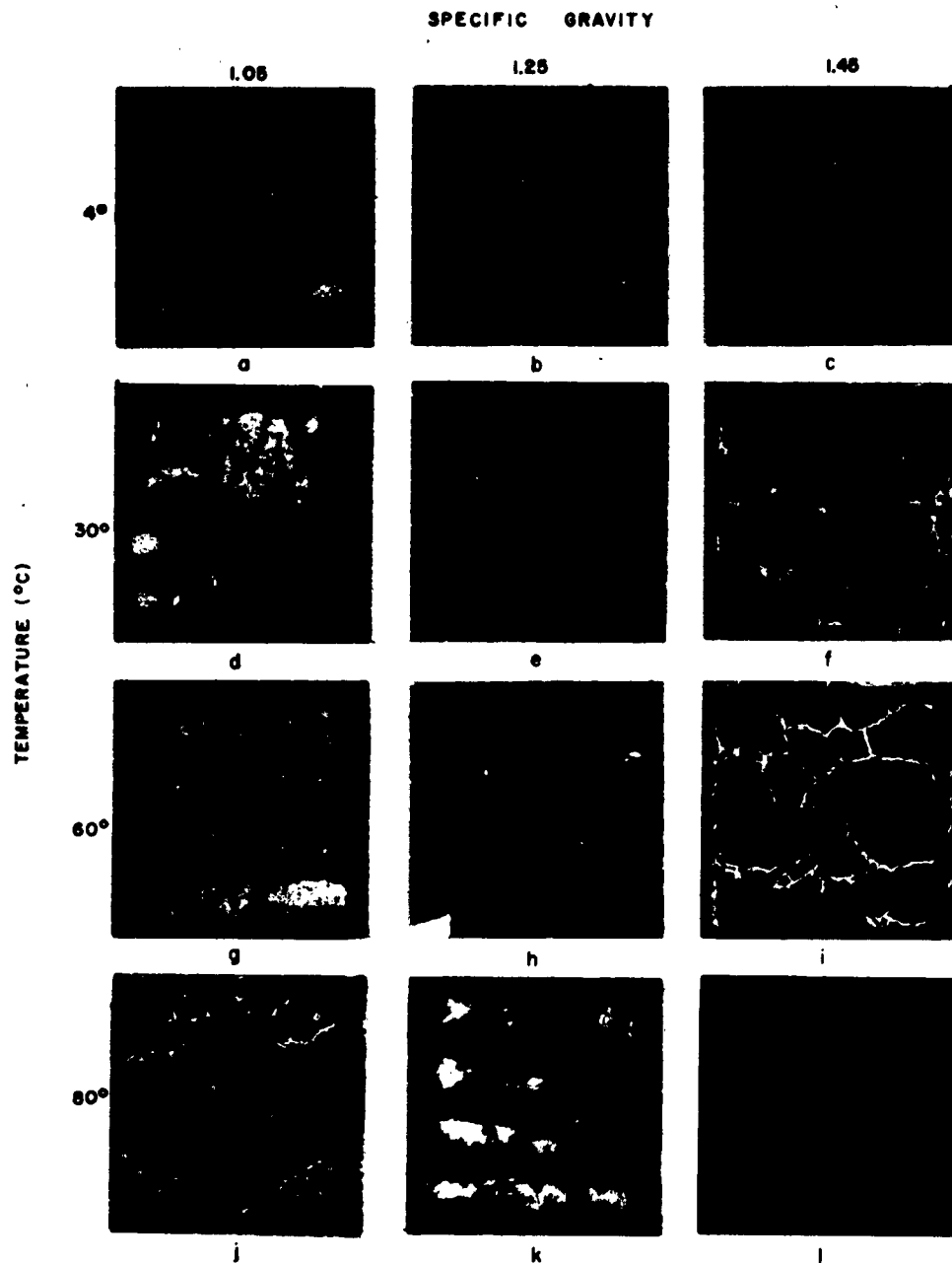


Fig. 25 - Appearance of negative plates formed at a current density of 0.23 amp/dm^2 . Note the heavily sulfated cracks in the samples (f), (i), and (j). See also Fig. 26. 2.8X magnification. (Reduction in printing approximately 20%.)

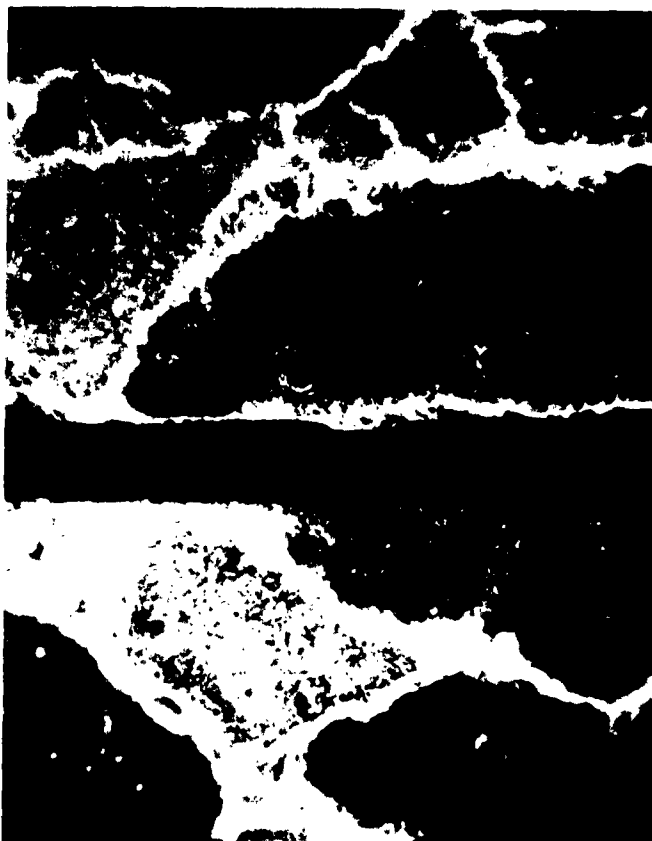


Fig. 26 - A slightly more magnified area of Fig. 25(i). This view gives a better idea of the heavy sulfation occurring in the cracks of the plate. 13X magnification.

Appearance at High Magnification - In general, the behavior was much like that at the lower current density. The lowest temperature and the lowest specific gravity of the electrolyte produced the largest needlelike crystals. Increasing the temperature had little effect except to make the crystals slightly smaller. Increasing the specific gravity of the electrolyte converted the crystals to coarse, roughly spherical grains. Under equivalent conditions of temperature and specific gravity, however, the particles formed at the higher current density were consistently smaller than those formed at lower current density. Compare, for example, Figs. 22 and 23 with Figs. 27 and 28.

Plates Formed at 2.3 amp/dm²

Appearance at Low Magnification - The area covered by the formed material can be seen by reference to Fig. 29. The samples formed at low and intermediate temperatures in the lower specific gravities, and for specific gravities at the lowest temperature of 4°C, showed a pronounced tendency to confine the reaction to an area immediately surrounding the grid and along the sides of cracks, Fig. 30. At the highest temperature for all specific gravities, and for all but the lowest temperature at the highest specific gravity, the same sulfation along the cracks that was previously referred to became very pronounced and forming did not appear to take place along cracks and at the grids as had been usual at

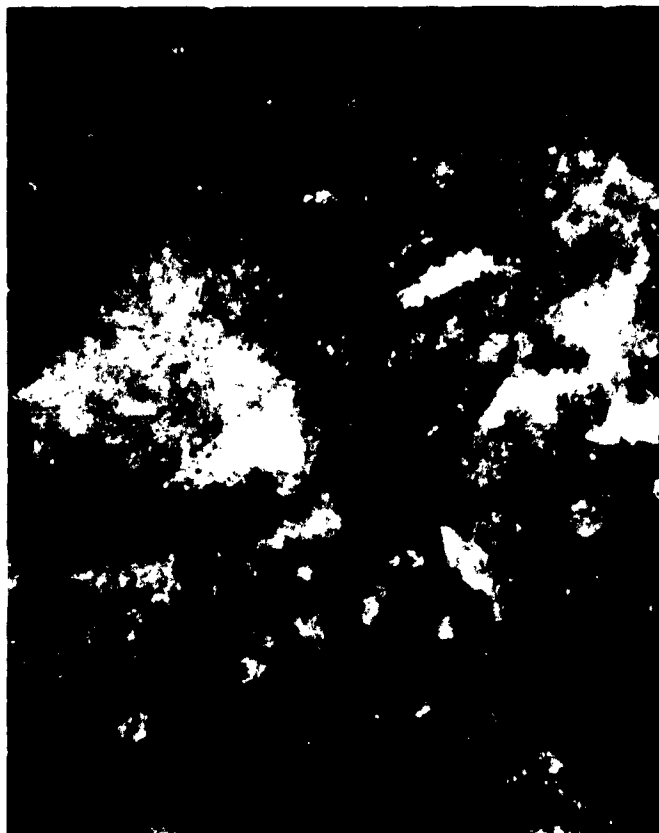


Fig. 27 - The appearance of needlelike crystals of lead formed at a current density of 0.23 amp/dm^2 , an acid specific gravity of 1.05, and a temperature of 4°C . Note that these crystals are smaller than those shown in Fig. 22 from a plate formed under the same conditions, with the exception of a lower current density. 1000X magnification.

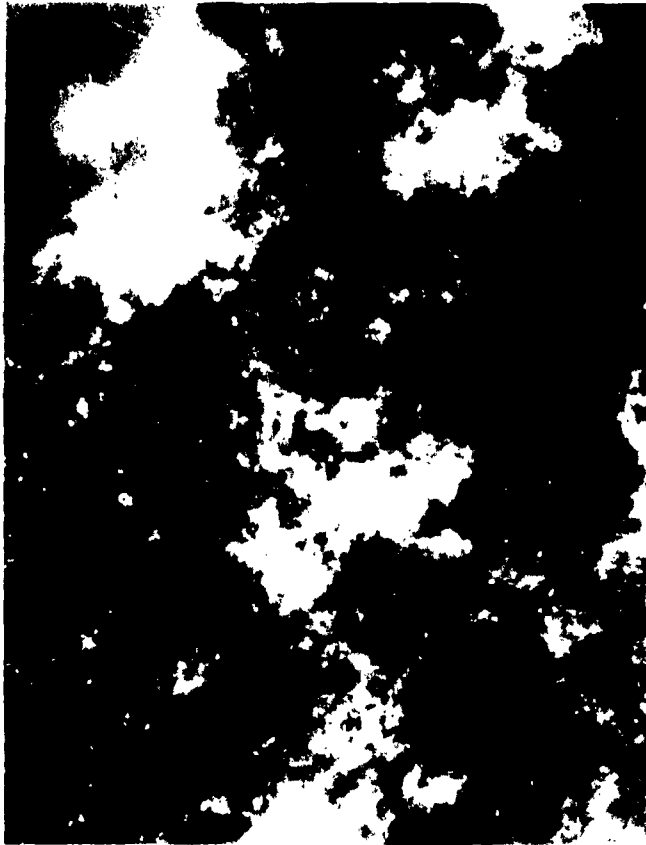


Fig. 28 - The appearance of lead formed under the same conditions as noted for Fig. 27, except that the specific gravity was increased to 1.45. Note the absence of needlelike crystals, the roughly spherical shape of the lead particles, and their size in relation to those of Fig. 23, which shows a plate formed under the same conditions, except at a lower current density. 1000X magnification.

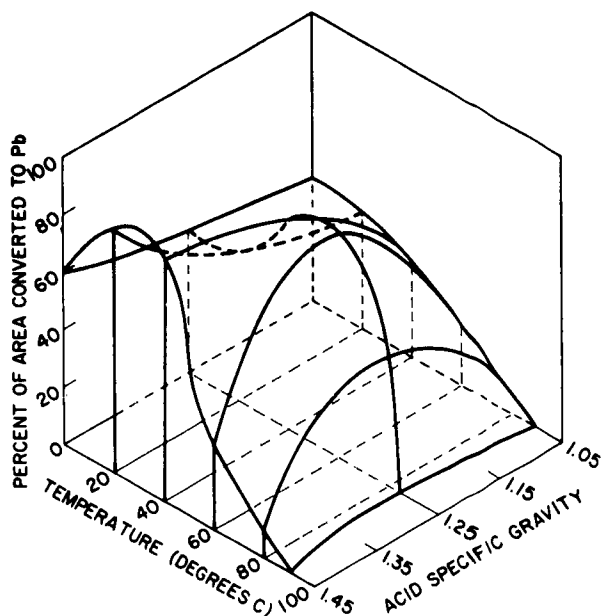


Fig. 29 - The relative area of the negative plate converted to lead at different temperatures and specific gravities of electrolyte when a current density of 2.3 amp/dm^2 was used. All samples received the same total current. Compare with Figs. 20 and 24.

lower current density and lower temperature. Forming appeared to be confined to certain regions that were surrounded by cracks and in contact at some point with the grid, Fig. 30. Only the areas in the photograph that have the darkest color consist of formed lead, the lighter areas remain unformed even though they appear much darker than in the original plate as received. This darkening is caused by the lead sulfate crystals becoming translucent, as was mentioned previously.

Examination at High Magnification - The remarks made for the previous current density group can be repeated almost exactly. Again the lowest temperature and lowest specific gravity produced the largest needlelike crystals. Increasing the temperature had slightly more effect than in the previous case since at the highest temperature the coarse, roughly spherical grains began to appear among the dendritic type. Increasing the specific gravity at a given temperature resulted in the same coarsening of structure and conversion to spherical particles that was described for the lower current density group. Under equivalent conditions of temperature and specific gravity the particles formed at this current density were consistently smaller than those formed at lower current density. Compare, for example, Figs. 22, 27, and 31 and Figs. 23, 28, and 32.

Summary

The lowest temperature, lowest specific gravity, and lowest current density produced the largest needlelike crystals. Increasing the specific gravity of electrolyte appeared to have the greatest effect on this structure, converting it to coarse spherical grains. Temperature appeared to have very little effect on structure, except to make the crystals slightly smaller. The same was true to increasing the current density. The most extensive area of formation occurred when the dendritic, needlelike crystals were present, but appeared to be more extensive when these were small than when they were very large. High specific gravity electrolyte and/or high temperature produced either shedding of the active material or an extensive sulfation in the cracks of the plate to such an extent that it appeared to interfere with formation.

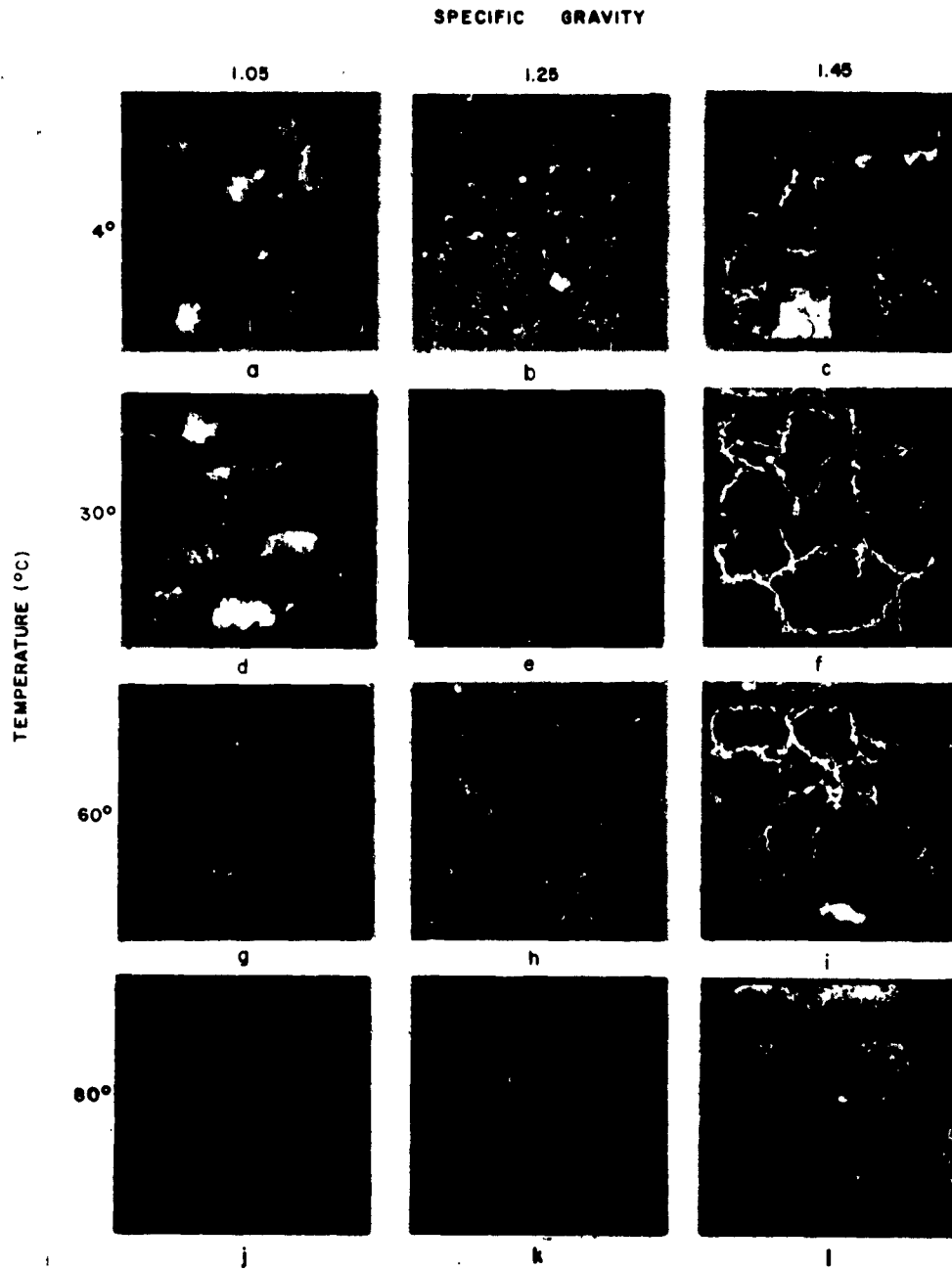


Fig. 30 - The appearance of negative plate material formed at a current density of 2.3 amp/dm² and at the temperatures and specific gravities indicated. Compare with Figs. 21 and 25. 2.8X magnification. (Reduction in printing approximately 20%.)



Fig. 31 - Small crystals of lead formed when the current density was 2.3 amp/dm^2 , the temperature 4°C , and the electrolyte specific gravity 1.05. Compare with Figs. 22 and 27. 1000X magnification.



Fig. 32 - Small spherical lead crystals formed when the conditions were as given for Fig. 31, except that the specific gravity was increased to 1.45. Note the change from needlelike to spherical crystals. Compare also with Figs. 23 and 28. 1000X magnification.

DISCUSSION

The reader is warned against making generalizations as to plate behavior on the basis of the following observations and conclusions which are based upon examination of samples submitted by one manufacturer only. While it is probable that other paste compositions will produce the same reactions in varying degree, no evidence as yet has been presented that this is so.

In the case of the positive plate the process of formation appeared to take place preferentially upon the surface of certain crystals present in the paste and then afterwards spread to crystals of an apparently different type. It was originally believed that these crystals which nucleated the formation of lead dioxide existed in the original dried paste, and the first report of this series (1) carried a statement to that effect. However, the inability to find these crystals in the unformed plates and their subsequent presence even in the unformed parts of the plate after being subjected to test conditions, as well as the manner in which their shape and size are influenced by the environment of the process, argue strongly that they are formed during passage of the electric current, before the formation of any lead dioxide. This may be the result of concentration gradients set up by the passage of the current or of the formation of an entirely new compound such as a basic sulfate.

Either because of a more favorable physical condition or because they constitute a new compound, these crystals initiate the formation of lead dioxide. A study of these many samples has demonstrated that the process of formation begins with crystals of this type that are in contact with the grid; formation never occurs spontaneously at points where this contact is not established. From the original crystals in contact with the grid the process continues to spread through the paste from one to another of these crystals at points of contact. Simultaneously, the process is transferred, but at a slower rate, to an apparently different type of crystal which forms the bulk of the paste. This latter crystal seems to be insensitive to changes in forming conditions, maintaining throughout the same small size and roughly spherical shape.

Depending upon the conditions under which forming takes place, the crystals upon which the lead dioxide preferentially forms may be long and needlelike dendrites or regular polyhedrons. The forming process may convert only the surface of the crystal to the hard and dense lead dioxide, leaving the balance of the crystal converted to the softer form, or alternately the entire crystal may be converted to the hard dense form. The determination of the reason for this difference was beyond the scope of this investigation but is surely dependent upon the conditions under which forming takes place.

The presence of crystals of the type referred to above does not appear absolutely necessary to initiate the conversion to lead dioxide, but it is significant that very little formation took place in the absence of these crystals (all samples received the same total current).

The hard, dense lead dioxide that stands in relief in the photographs represents the outlines of the original lead sulfate crystals on which the dioxide formed. It is very interesting to note that lead sulfate crystals, of a size and shape corresponding to the forms found in the area where conversion had taken place, were always found in that part of the same plate that had not yet been converted, i.e., rarely was a formed lead dioxide crystal found that did not correspond to an unformed lead sulfate crystal.

This makes a very good basis for the assumption that the entire process is a solid state reaction since it appears that the original crystal, whether lead sulfate or a basic sulfate of lead, is being converted into lead dioxide without external change in form. This would not be the case if any type of solution or redepositon was taking place.

The structure of the positive plate might have extreme importance when considering the problem of battery efficiency and longevity. The efficiency of the process depends upon the ease with which electrolyte can penetrate into all parts of the active material and upon the ability of the active material to conduct the electric current to and from the grid. The longevity of the plate depends to a large extent upon the ability of the positive active material to resist shedding or the gradual washing away of the lead dioxide particles. It has long been believed that lead sulfate acts as a binder or cement to hold the plate together. In the fully charged plate the amount of lead sulfate present must be extremely small and with each succeeding cycle would not only become less but would be converted to large particles which would have little tendency to act as a binder. It has been seen that the formed material consists of hard dense particles and softer, more loosely packed particles. The hard, dense areas are probably excellent conductors of electricity but, being dense and relatively nonporous, resist any further reaction except perhaps at the surface. The soft, loosely packed particles are probably not very conductive but are probably very reactive because they not only contain spaces between them but each particle itself appears soft and porous. Under certain conditions, as when the crystals are long and needlelike or when rectangular crystals have a coating of the hard lead dioxide on their exterior, Figs. 4 and 13, these hard, dense formations form either a fiber structure or a cell-like network throughout the active material. This could conceivably act not only as a binder or retainer but also as a conductor for the mass of more porous and reactive crystals which make up the bulk of the plate.

Assuming the correctness of these suppositions the ideal paste composition would be one that would result in the formation of a large number of dendritic or rectangular crystals upon which the subsequent forming would produce a hard, dense coating of lead dioxide which thus would form an interconnecting network throughout the remainder of the active material. This latter would be in a softer, more porous, and more reactive condition. The harder lead dioxide network would act as a support for the softer material and conduct the electric current necessary for the reaction but would itself react so slowly as to assume its continuation throughout the discharge cycle. This same cycle, however, would cause the conversion of the more reactive (softer) material to lead sulfate. Presumably there would also be an optimum ratio of hard to soft dioxide in order to achieve maximum efficiency and durability without loss of either. The extent of the present investigation is insufficient to determine the correctness of the above assumption.

From the standpoint of determining the most efficient conditions for the forming of the positive plate, these conditions were probably not reached. The trend shown by Figs. 1, 10, and 16 indicate that even lower current densities and specific gravities might have been used with more success. The use of lower specific gravities might be desirable, but from the standpoint of practical application it should be noted that the lowest current density used in this experiment would require ten times as long to completely form a plate as does the process used in industry at present.

Only actual capacity tests could have been used to determine the total effective amount of formed material for each varied forming condition. Such tests were, unfortunately, not included in this experiment. However, on the basis of close examination, it is believed that those samples which had the greatest area of formed material also represented the greatest actual amount in terms of weight. It is further believed that with the form of crystal and type of distribution present in the samples of greatest area of lead dioxide, the plate was in the best condition to continue additional formation at maximum efficiency.

There is one additional point that should be discussed. The variations in structure were most noticeable very close to the grid member. As one continued to examine the surface at greater and greater distances from the grid it was found that the structure became less and less influenced by changes in operating conditions and tended to revert more and more to a coarse and irregular structure as in Fig. 14. Evidently, as the reaction became diluted by distance, resistance, and time it tended also to be less influenced by changes in its environment.

This was not the case in the negative plate where the same type of structure could be found in any part of the plate where formation had occurred. The process in the negative undoubtedly involves solution and redeposition. Not only was a change observed in the appearance of the lead sulfate just ahead of where formation had already taken place, but the lead crystals apparently formed in an area from which the sulfate had dissolved, and these lead crystals were observed to be surrounded by a clear space. Examination at the edge of formed areas indicated that formation progressed into unformed areas through the simultaneous growth of a number of dendritic filaments of lead. As in the positive, this process had to be initiated at the grid member, but thereafter any crystal already formed could initiate the growth of new crystal. Unlike the case with the positive plate, no special type of crystal seemed necessary for formation to take place.

The most efficient condition for negative plate operation would appear to be the one where maximum dendritic structure was present, i.e., with the crystal type producing the maximum porosity and surface area. The least efficient would be that where a granular type of lead crystal was present.

The negative appeared capable of rather efficient forming over a wider range of operating variables than did the positive, and it was not as sensitive to changes. A fairly sharp line could be drawn, upon one side of which the dendritic type structure prevailed and upon the other, the granular type. The greatest area of formed material accompanied the growth of the dendritic type crystal. It is somewhat surprising that very long and large dendrites did not appear to be as effective as those somewhat smaller in size.

The eventual failure of the negative plate is not caused by loss of active material or by corrosion of the grid, as in the positive, but by growth of lead sulfate crystals in the pores of the plate to such a size as to completely block the ingress of electrolyte. This is coupled with a gradual conversion of the long, needlelike dendritic crystals of lead into a more nearly spherical form with a consequent smaller surface area. This degradation of the plate is largely brought about by the continual solution and redeposition of crystals that takes place as the plate cycles, and there does not appear to be any permanency to the structure produced during forming. Consequently, it does not appear that negative plate longevity or efficiency can receive any permanent improvement from the method of forming, although the initial performance could undoubtedly be much influenced by this means.

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2. Simon, A.C., and Jones, E.L., "Investigation of Storage Battery Failure by a Method of Plastic Impregnation," J. Electrochem. Soc. 102:279 (1955); "New Techniques for Applying the Microscope to Problems of Battery Research and Development," NRL Report 5149, June 25, 1958

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<p style="text-align: center;">UNCLASSIFIED</p> <p>Naval Research Laboratory. Report 5733. AN INVESTIGATION OF ELECTRODE PROCESSES BY MICROSCOPY. PART 2 - THE MICROSTRUCTURE OF LEAD DIOXIDE AND SPONGE LEAD PLATES AS INFLUENCED BY DIFFERENT TEMPERATURES, ELECTROLYTE SPECIFIC GRAVITIES, AND CURRENT DENSITIES IN THE FORMING PROCESS, by A. C. Simon and E. L. Jones. 40 pp. and figs., February 1, 1962.</p> <p>In separate experiments battery plates were formed at specific gravities of electrolyte ranging from 1.05 to 1.45, at temperatures from 4° to 80°C, and at current densities from 0.023 to 2.3 amp/dm² (approximately 0.23 to 23 amp/ft²). The time of forming was adjusted in each case so that all samples received the same total current. This total current was 1/4 that required for complete formation of a similar plate under the</p>	<p style="text-align: center;">UNCLASSIFIED</p> <p>Naval Research Laboratory. Report 5733. AN INVESTIGATION OF ELECTRODE PROCESSES BY MICROSCOPY. PART 2 - THE MICROSTRUCTURE OF LEAD DIOXIDE AND SPONGE LEAD PLATES AS INFLUENCED BY DIFFERENT TEMPERATURES, ELECTROLYTE SPECIFIC GRAVITIES, AND CURRENT DENSITIES IN THE FORMING PROCESS, by A. C. Simon and E. L. Jones. 40 pp. and figs., February 1, 1962.</p> <p>In separate experiments battery plates were formed at specific gravities of electrolyte ranging from 1.05 to 1.45, at temperatures from 4° to 80°C, and at current densities from 0.023 to 2.3 amp/dm² (approximately 0.23 to 23 amp/ft²). The time of forming was adjusted in each case so that all samples received the same total current. This total current was 1/4 that required for complete formation of a similar plate under the</p>	<p style="text-align: center;">UNCLASSIFIED (Over)</p> <p>1. Electrodes - Production</p> <p>2. Lead - Microstructure</p> <p>3. Lead oxides - Microstructure</p> <p>I. Simon, A. C.</p> <p>II. Jones, E. L.</p>
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