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H. H. WHEELER ET AL

2,194,189

POLE LINE INSULATOR

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FIG. 1

*SURFACE LAYER OF HIGH
ELECTRICAL RESISTIVITY
AND HIGH INTERFACIAL
TENSION WITH WATER*

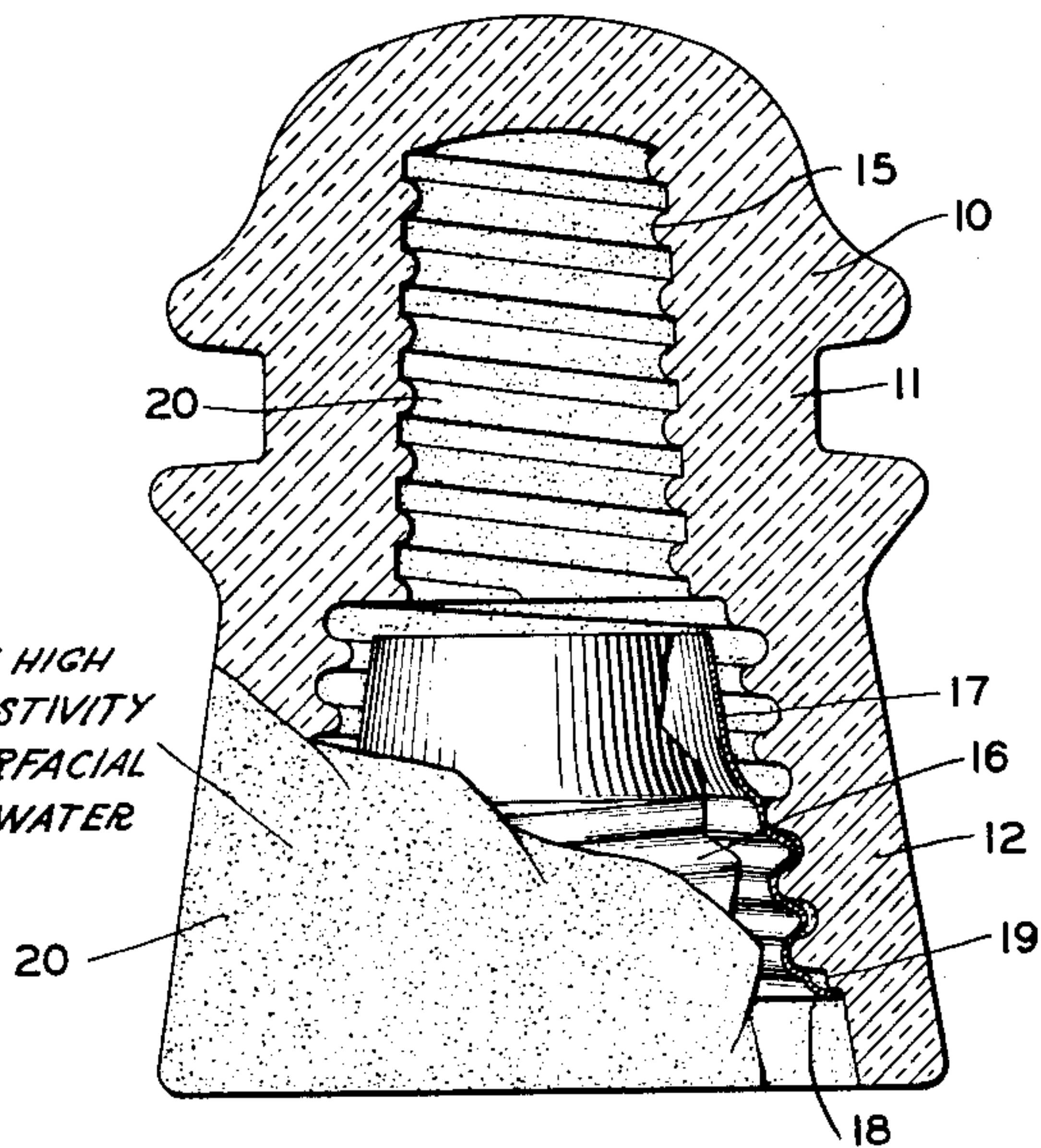
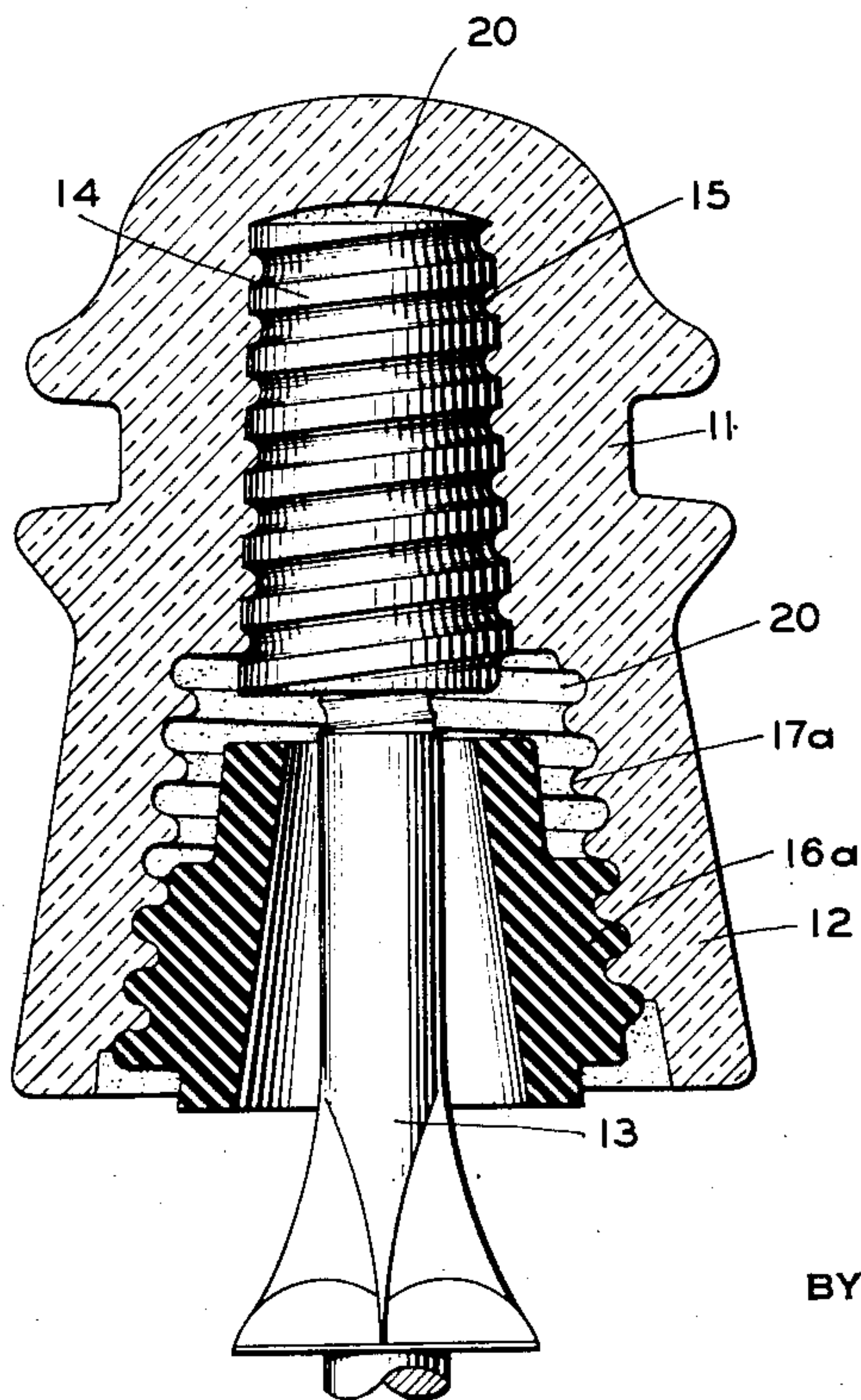


FIG. 2



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2,194,189

POLE LINE INSULATOR

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Application May 5, 1936, Serial No. 78,054

18 Claims. (Cl. 174—209)

This invention relates to electrical insulators and more particularly to pole line insulators for telegraph and other communication circuits, and is an improvement on the invention disclosed in the copending application of Herbert H. Wheeler and Orris McGinnis, Ser. No. 621,478, filed July 8, 1932, now Patent No. 2,165,773, dated July 11, 1939.

As stated in the aforesaid pending application, in communication circuits the signaling currents usually are of small amplitude and a definite and considerable part of each impulse is required to effect the operation of the relays or other receiving apparatus. Repeaters are disposed at convenient locations, but in some instances the repeater points are widely separated and the signals reaching the receiving apparatus may become highly attenuated. Consequently, the margin on a telegraph line under the most favorable conditions is relatively small and any loss in signaling current due to leakage may seriously interfere with the proper operation of the system. Such lines, furthermore, are often disposed along highways and railroads in common with other signaling and power lines, and are subject to interference therefrom, and a considerable portion of the signaling current is required to override these interfering or transient currents, thereby further reducing the margin. It is highly essential, therefore, that pole line insulators in addition to providing adequate support should interpose a very high resistance to leakage of current from the conductor to earth or to adjacent conductors, and to perform this function properly the insulator must maintain this high insulating resistance under the most adverse weather conditions. The materials heretofore found most suitable for insulators are vitreous materials, such as glass and porcelain. All of these materials, when dry and clean, provide a negligible leakage path for the signaling current, but when exposed to moisture they are subject to considerable surface leakage. It is possible to construct the insulators of such shape that even during heavy rains there will be a certain amount of substantially dry surface in the leakage path from the conductor to the pole, this usually being obtained by providing the insulator with concentric petticoats having an annular reentrant recess therebetween, and in some cases by providing a splash guard between the insulator and the supporting pin so as to prevent entrance of moisture into the interior of the insulator. By means of such construction, leakage occurring across clean insulators due to rain

alone has been materially reduced. However, the most severe condition of surface leakage in insulators as heretofore made does not occur, as might be supposed, during heavy rain, but occurs in extremely humid weather, at which time the moisture condenses on both the interior and exterior surfaces of the insulator and forms a substantially continuous leakage path between the conductor and supporting cross arm or pole and thence either to ground or to adjacent conductors.

The invention in the aforesaid Wheeler and McGinnis application is based upon the discovery that an insulator, the surface of which has been treated, as by spraying, while hot with certain compounds of metals, offers a much greater resistance to the passage of leakage currents in rainy and humid weather than insulators which are not so treated.

One of the objects of the present invention is to simplify the process of producing an insulating surface layer on insulators of the foregoing character, and to ensure greater uniformity in the product.

Another object is to reduce the amount of residue remaining on the insulators after they have been sprayed or otherwise treated with the compounds which form the insulating surface layer.

Another object of the invention is to provide a pole line insulator of the foregoing character with a surface layer having a higher resistance to leakage than has heretofore been obtainable.

A further object is to provide a more permanent surface layer exhibiting the desired high resistance to leakage, thereby to greatly increase the useful life of the insulator.

An additional object is to further increase the interfacial tension of the insulator surface with water, and thus more effectively prevent the formation of moisture films thereon.

Other objects and advantages of the invention will hereinafter appear.

Referring to the drawing:

Fig. 1 is a view, partly in section, of a pole line insulator treated in accordance with the present invention, and provided with a protective bushing, and

Fig. 2 is a sectional view of the insulator applied to its supporting pin and provided with another form of protective bushing.

The insulator 10 preferably, although not necessarily, is composed of a vitreous material, such as glass, and is of a conventional form in common use for telegraph pole lines. It has the usual annular groove 11 in its periphery for the

reception and anchorage of the line wire. In the form shown, the insulator is provided with a single skirt 12, although it is to be understood that it may be of any desired shape; for instance, it may be provided with the well known form of double petticoat. It is supported on a pin 13, Fig. 2, shown in the present instance as comprising a steel spindle, with an insulating cob 14 threaded thereon, the cob in turn being threaded to the inner recess 15 of the insulator, although the pin may be directly threaded to the glass if desired. In the form illustrated the skirt portion 12 is also threaded for the reception of a protective bushing 16, Fig. 1, or 16a, Fig. 2, which surrounds the pin 13 out of contact therewith, the member being formed at 17, Fig. 1, or 17a, Fig. 2, to provide an annular recess between the body of the insulator and the skirt portion 12, this recess being disposed out of the line of entrance of dirt and other foreign matter into the insulator, and therefore is in such position that accumulations of dirt therein are minimized. As indicated in Fig. 1, the protective bushing may be formed from sheet metal, or as shown in Fig. 2, may comprise a bushing of insulating material thereby increasing the surface leakage path between the wire anchoring groove 11 and the cob 14. In the form shown in Fig. 1, the metal bushing has a lower resilient flanged portion 18 which engages a shoulder portion 19 of the skirt 12 to thereby spring the flanged portion into frictional engagement with the skirt to prevent the bushing from working loose in service, and to provide a close fit to prevent circulation of air in the recess between the bushing and insulator. It is to be understood that the protective bushing 16 may be omitted if desired. Preferably, as indicated by the stippled areas 20 in Fig. 1, both the inner and outer surfaces of the insulator are treated by the application thereto of compounds of metals hereinafter described.

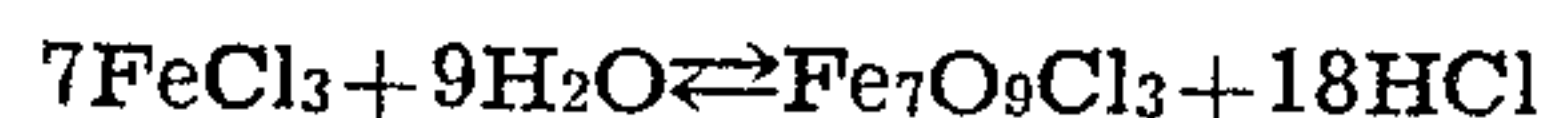
As set forth in the aforesaid copending application, one process of applying the compounds of metals to the surface of the insulator may be similar to that which has been employed in the glass industry for coloration purposes, although for the purpose of the invention of the aforesaid application it is necessary to observe certain precautions and in some respects to modify the process to obtain the required service characteristics of the insulator. The process consists in directing a fine spray of aqueous solutions of certain compounds of metals onto the heated surface of the insulator when such surface is at a temperature of between 700° and 1300° F., the spraying operation usually being performed just after the insulator has been removed from the mold, this operation being carried out in a normal atmosphere. After spraying, the glasses may be annealed in the regular manner, which annealing does not appear to influence the treatment.

The beneficial effect obtained by the coating appears to be due to the extremely high interfacial tension of the treated surface with water, by reason of which when moisture is condensed on the surface of the insulator it is subsequently caused to assume a globular form and therefore a discontinuous layer. Capillary tests of treated surfaces show them to have positive or convex meniscus characteristics similar to that between ordinary glass and mercury due to which the water does not wet the surface of the treated glass. The treated surface appears to be a layer

or coating comprising the substances applied thereto dispersed throughout the outside layer of glass. The exact physical chemical nature of the coating is extremely difficult to determine. With certain of the compounds hereinafter disclosed, it may consist chiefly of an oxide of the metal or metals employed dispersed in the glass surface while with other compounds it appears to consist chiefly of a basic chloride in dispersion, and in certain combinations of compounds, especially the hydrosols, it appears to be a combination of basic chlorides of the metals employed dispersed in the glass surface. In every case the non-conducting coating appears to be either the oxide or the basic salt of the corresponding metal salt, e. g., basic metal sulphate, basic metal chloride, etc., dispersed in the glass surface of the insulator.

While insulators treated in the manner disclosed in the aforesaid Wheeler and McGinnis copending application have generally proved satisfactory, the process has the disadvantage in that there is a lack of uniformity in the product which results in a high percentage of rejections and thus materially increases the cost of producing the insulators. Also, insulators made in the manner heretofore employed have had an undesirable amount of residue remaining thereon after the spraying operation, which residue is difficult to remove and in some cases can not be satisfactorily removed.

Analyses of the coatings on the surfaces of the insulators disclosed that when an aqueous solution of iron chloride is employed, basic chloride of iron is a component of the dispersion medium of the iridescent coating. These analyses indicated the following reaction of the hot surfaces of the insulators as the ferric chloride aqueous solution contacted the insulators in spray form:



Further analyses made of coatings formed by spraying a ferric chloride aqueous solution on hot glass insulator surfaces disclosed that the general reaction going forward on the hot glass surface is a hydrolysis from which results a dispersion in glass of chloride of iron.

The general stoichiometrical equation describing the chemical reaction on the hot glass surface may be written as follows:



Iridescent coatings results when ferric chloride aqueous solutions are sprayed on hot glass surfaces because of the strong tendency of ferric chloride to hydrolyze particularly at elevated temperatures. It is well known that ferric ions are practically colorless. However, an aqueous solution of a ferric salt generally shows a yellow brown color because of the small amount of hydrolysis naturally occurring when ferric chloride is dissolved in cold water. This hydrolysis is materially increased when an aqueous solution is heated to about 200 deg. F. as is shown by the deepening of the brown color when an aqueous solution of a ferric salt is heated. This strong tendency of ferric salts to hydrolyze in contact with very hot water explains the formation of iridescent coatings when ferric chloride aqueous solutions are sprayed onto hot glass surfaces.

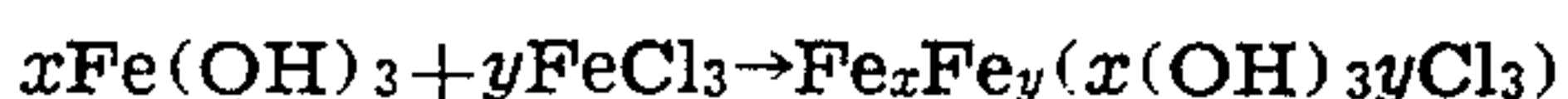
The amount of basic chloride of iron which is retained on the glass as disperse phase in the iridescent coating is the sum of the cold hydrolysis in aqueous solution plus the hot hydrolysis resulting when the aqueous ferric salt solution

spray hits the hot glass surface. Although the above reaction equation accurately represents the amount of chloride of iron retained in the iridescent coating as a result of both the cold and hot hydrolysis, it in no way indicates the percentage of the ferric chloride in the solution which enters into the hydrolysis reaction. Inasmuch as ferric chloride sublimes at a much lower temperature than the temperature of the heated glass surface during the iridizing process most of the ferric chloride never hydrolyzes, but instead simply sublimes. This necessitates the use of highly concentrated ferric chloride solutions in order to achieve enough hydrolysis to obtain iridescence.

We have found that the reaction shown in the above stoichiometrical equation may be effected prior to the spraying of the heated glass by preparing hydrosols of the compounds of metals, and substantial advantages obtained thereby. First, the heated glass is relieved of the work of hydrolyzing the iron chloride or other compound employed and as a consequence better coatings are obtained. Second, while the equation shows the reaction occurring on the hot glass surface, it does not show what part of the chloride hydrolyzes. In the case of iron chloride it appears that a large part of it sublimes without decomposition and is therefore wasted. Since the basic chlorides obtained from the hydrosols do not sublime, the only loss in using the hydrosol is that part of the spray which does not come in contact with the hot glass.

In order to make practical spraying solutions of the hydrosol type, all of the components of the solution, with the exception of the basic salt of the metal, should be volatile. Several different methods of preparing such hydrosols, e. g., an iron hydrosol, are as follows:

(1) Peptizing freshly prepared ferric hydroxide by means of normal ferric chloride to give basic chloride of iron hydrosol:



(2) Neutralizing most of the ferric chloride in aqueous solution by an alkali hydroxide and then dialyzing the alkali chloride by means of a parchment bomb immersed in water:



The NaCl is removed by dialysis.

(3) Neutralizing most of the ferric chloride in aqueous solution by a volatile hydroxide and using this solution without any further treatment:



The method used in the preparation of the hydrosols outlined under (3) above is preferred since it is the most simple and practical of the three. Furthermore the hydrosols prepared by this method are stable, and the basic chlorides produced are insoluble in water. Also the ammonium chloride is so highly volatile on the hot glass surfaces that no spray residue aggravation is encountered from this source.

Experiments have shown that a hydrosol gives as good a coating as the iron chloride chemical solution heretofore employed and with much less concentrated solution. For instance, a 10% concentration of iron hydrosol produces as good a coating in approximately the same spraying time as an 80% iron chloride solution. Also, the amount of residue is not only less but is more easily removed than in the case of the iron chloride coating.

Although iron is used for illustrative purposes, a large number of other metals may be used in preparing the hydrosols. For example, hydrosols of aluminum, tin, aluminum-tin, copper-tin, cobalt-tin, nickel-tin, cadmium-tin, chromium-tin, chromium-iron, zinc-tin, iron-tin, strontium-tin, barium-tin, calcium-tin, magnesium-tin and manganese-tin may be employed. In combination hydrosols, for example, of aluminum or copper with tin, hydrosols of aluminum or copper salts may first be prepared and the tin salt added to them, or the two salts may be put into solution together and the combination hydrosol made from this mixed solution. The latter method is preferable because of the fact that equilibrium occurs immediately whereas in the former method equilibrium is not attained until after the hydrosol has stood for some weeks. The final result, however, is the same in both cases. In substantially all of the foregoing cases iridescence is not obtained and is not essential to the surface characteristics for producing the desired electrical effects.

It will be noted that all of the foregoing, with the exception of the hydrosols of a single metal and the chromium-iron, are combinations of tin plus another metal. It is possible, however, to make another series, say with chromium, in combination with a number of other metals. It appears that an essential characteristic of these combination hydrosols is that at least one of the metal salts used have the property of hydrolyzing readily. Also, anions other than those cited for illustrative purposes may be used, such as sulphates, nitrates, acetates, etc.

While insulators treated in the manner disclosed in the above mentioned copending application have in general proved satisfactory the present invention also contemplates an insulator having a surface layer which exhibits a higher resistance to leakage than that heretofore obtained, and also exhibits a greater permanency and thus materially increases the useful life of the insulator. This latter feature is especially important in the case of insulators on telegraph pole lines which are located along railroads or other places where they are subject to acid fumes or other conditions tending to dissolve or destroy the high resistance surface layers or coatings thereon; it also enables the insulator to withstand severe weathering without having the insulating surface layer diminished or deleteriously affected thereby. For this purpose the surface layer is formed from a combination of at least two compounds of metals, one of which compounds causes the layer to have high electrical resistivity and the other of which causes the layer to have high permanency and preferably high interfacial tension with water.

A compound which we have found especially suitable for giving the desired permanency to the coating is tin chloride. The strongest acids have but slight effect upon a coating resulting from the use of either stannous or stannic chloride (stannic chloride being preferred), whereas certain acids will remove other coatings, such as iron chloride, within a few hours. Another desirable characteristic of a tin chloride coating is its extremely high interfacial tension with water, this being important because it is the high interfacial tension that prevents the formation of moisture films and enables the surface to retain its high resistance. A still further desirable characteristic is the ease of application of the tin chloride solution since the hot glass surfaces

readily acquire the coating as the solution is sprayed on them, and extreme care and perfect conditions, except as they pertain to the glass itself, are not necessary to produce good results.

Thus a more uniform product, with fewer rejections and consequently lower cost, is obtained.

A disadvantage of tin chloride, however, lies in the fact that while very thin coatings thereof are substantially nonconducting, when heavier coatings are employed to give the necessary permanency the same become more conducting as the thickness of the coatings increases and this reduces the insulation value of the coatings. We have discovered that this disadvantage of a tin chloride coating may be overcome, and all its advantages retained, by applying a solution of tin and iron chlorides. This combination or mixture is more easily applied than one composed of iron chloride alone and produces a coating which is more permanent and has more satisfactory insulating surface characteristics than was heretofore obtainable. Furthermore, the spray residue is more easily removed.

A preferred coating is obtained with a combination of ferric and stannic chlorides. As for permanency, coatings obtained by the use of the iron-tin combination have shown themselves superior to the iron chloride and iron hydrosol coatings.

In addition to the foregoing, various other compounds may be employed in combination with tin, e. g., ferric acetate, ferrous nitrate, chromium acetate, aluminum chloride, aluminum nitrate, nickel acetate, nickel chloride, zinc acetate, zinc nitrate and copper acetate.

The various foregoing compounds may also be combined with a metal other than tin, for example, chromium, so long as the metal causes the insulating layer to have the desired high permanency and high interfacial tension with water.

As above stated, the exact physical chemical nature of the various coatings is difficult to determine. When a solution of iron chloride alone is employed, the surface layer comprises an insoluble basic iron chloride dispersed in glass; when tin chloride is used, the surface layer appears to consist principally of an oxide dispersion in glass since the chloride of tin is not so stable and probably changes to an oxide. In the iron-tin hydrosol the coating appears to be a basic chloride dispersion in glass. The final result depends principally upon the stability of the basic compound of the metal or metals employed.

Regarding the spray residue which is found on the surfaces sprayed with either the foregoing salt solutions or the hydrosols, before the non-conducting coating displays the phenomenon of high interfacial tension with water, this residue must be removed. This may be done by washing or otherwise treating the surface with a strong soap solution or other detergent and rinsing in clean water. To obtain a complete removal of the residue, it is sometimes necessary to use a washing cloth or scrubbing brush so that mechanical action is applied in addition to the washing.

For brevity in the specification and claims, the term "compound" is used in a generic sense to define chemical and other compounds formed by the union or mixture of elements and ingredients; and the term "solution" includes chemical solutions, colloidal solutions and suspensions.

Various substances and combinations of substances other than those specifically mentioned hereinbefore may obviously be employed without departing from the invention, and the invention therefore is not limited except as indicated by the scope of the appended claims.

We claim:

1. An insulator for electrical conductors comprising a body having a surface layer of high electrical resistivity, high permanency and high interfacial tension with water, said surface layer comprising a basic chloride produced by applying to the surface of the insulator body while at a high temperature a hydrosol of a chloride of a metal.

2. An insulator for electrical conductors comprising a body having a surface layer of high electrical resistivity, high permanency and high interfacial tension with water, said surface layer comprising a compound produced by applying to the surface of the insulator body while at a high temperature a hydrosol of tin and iron.

3. An insulator for electrical conductors comprising a body having a surface layer of high electrical resistivity, high permanency and high interfacial tension with water, said surface layer comprising a compound produced by applying to the surface of the insulator body while at a high temperature a hydrosol of iron chloride and tin chloride.

4. An insulator for electrical conductors comprising a body having a surface layer of high electrical resistivity, high permanency and high interfacial tension with water, said surface layer comprising a compound produced by applying to the surface of the insulator body while at a high temperature a hydrosol of ferric chloride and stannic chloride.

5. An insulator for electrical conductors comprising a body of vitreous material having a surface layer of high electrical resistivity, high permanency and high interfacial tension with water, said surface layer comprising a mixture of at least two compounds of metals produced by the hydrolysis of salts of a group consisting of acetates, nitrates, chlorides and sulphates of the metals, one of which compounds causes the layer to have high permanency and high interfacial tension with water.

6. An insulator for electrical conductors comprising a body of vitreous material having a surface layer of high electrical resistivity, high permanency and high interfacial tension with water, said surface layer comprising a mixture of at least two compounds of metals produced by the hydrolysis of salts of a group consisting of acetates, nitrates, chlorides and sulphates of the metals, one of which compounds causes the layer to have high electrical resistivity and the other of which causes the layer to have high permanency.

7. An insulator for electrical conductors comprising a body of vitreous material having a surface layer of high electrical resistivity, high permanency and high interfacial tension with water, said surface layer comprising a mixture of at least two compounds of metals produced by the hydrolysis of salts of a group consisting of acetates, nitrates, chlorides and sulphates of the metals, one of which compounds causes the layer to have high electrical resistivity and the other of which causes the layer to have high interfacial tension with water.

8. An insulator for electrical conductors com-

prising a body of vitreous material having a surface layer of high electrical resistivity, high permanency and high interfacial tension with water, said surface layer comprising a mixture of at least two compounds of metals produced by the hydrolysis of salts of a group consisting of acetates, nitrates, chlorides and sulphates of the metals, one of said compounds causing the layer to have high electrical resistivity and both of said compounds causing the layer to have high interfacial tension with water.

9. An insulator for electrical conductors comprising a body of vitreous material having a surface layer of high electrical resistivity, high permanency and high interfacial tension with water, said surface layer comprising a mixture of at least two chlorides of metals of a group consisting of iron, tin, chromium, aluminum, nickel, zinc, copper, cobalt, cadmium, strontium, barium, calcium, magnesium, and manganese, one of said chlorides causing the layer to have high electrical resistivity and both of said chlorides causing the layer to have high interfacial tension with water.

10. An insulator for electrical conductors comprising a body of vitreous material having a surface layer of high electrical resistivity, high permanency and high interfacial tension with water, said surface layer comprising a mixture of at least two compounds of metals produced by the hydrolysis of salts of a group consisting of acetates, nitrates, chlorides and sulphates of the metals, one of said compounds tending to cause the layer to have low electrical resistivity, the other of said compounds causing the layer to have high electrical resistivity, and both of said compounds causing the layer to have high interfacial tension with water.

11. An insulator for electrical conductors comprising a body of insulating material having a surface layer of high electrical resistivity, high permanency and high interfacial tension with water, said surface layer comprising a compound formed by the hydrolysis of iron chloride and tin chloride.

12. An insulator for electrical conductors comprising a body of insulating material having a surface layer of high electrical resistivity, high permanency and high interfacial tension with water, said surface layer comprising a compound formed by the hydrolysis of iron chloride and stannic chloride.

13. An insulator for electrical conductors comprising a body of insulating material having

a surface layer of high electrical resistivity, high permanency and high interfacial tension with water, said surface layer comprising a compound formed by the hydrolysis of ferric and stannic chlorides.

14. An insulator for electrical conductors comprising a body having a non-iridescent surface layer of high electrical resistivity and high interfacial tension with water, said surface layer comprising a compound of a metal produced by applying to the surface of the insulator body while at a high temperature a hydrosol of a salt of a group consisting of acetates, nitrates, chlorides and sulphates of the metal.

15. A method of making an insulator having a surface layer of high electrical resistivity, high permanency and high interfacial tension with water, which comprises heating the body of the insulator to a high temperature and forming said surface layer by applying to the surface of the body when thus heated a hydrosol formed from a soluble salt of a group consisting of acetates, nitrates, chlorides and sulphates of a metal.

16. An insulator for electrical conductors comprising a body having a surface layer of high electrical resistivity, high permanency and high interfacial tension with water, said surface layer comprising a compound of a metal produced by applying to the surface of the insulator body while at a high temperature a hydrosol of a salt of a group consisting of acetates, nitrates, chlorides and sulphates of the metal.

17. An insulator for electrical conductors comprising a body having a surface layer of high electrical resistivity, high permanency and high interfacial tension with water, said surface layer comprising a mixture of at least two compounds of metals produced by applying to the surface of the insulator body while at a high temperature a hydrosol of salts of a group consisting of acetates, nitrates, chlorides and sulphates of the metals.

18. An insulator for electrical conductors comprising a body having a non-iridescent surface layer of high electrical resistivity and high interfacial tension with water, said surface layer comprising a mixture of at least two compounds of metals produced by the hydrolysis of salts of a group consisting of acetates, nitrates, chlorides and sulphates of the metals.

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