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PROCESS OF AND PRODUCT FOR PHOTOGRAPHIC ETCHING

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This invention relates to novel improvements in the art of photography, and it has particularly to do with a photographic film which has special advantages when used in the process of etching. The invention also pertains to a novel process of preparing the film and to the process of using and treating the film when employed, for instance, in etching and similar work.

The detailed description of the invention and its application and use will herein be made as bearing on the art of etching, although it is to be understood that the invention is not limited thereto. In this art of etching it is well understood the light sensitive film is known as a resist.

Various processes for transferring a light pattern upon a resist, developing the pattern in the resist by washing out that portion of the resist rendered insoluble by the light and etching the surface thus prepared, have been described and patented. There is also considerable suggestive and descriptive matter concerning these processes in various articles which have been published in the scientific journals. Of all the light sensitive substances which have been used, probably the most attention has been devoted to asphalt, and yet asphalt has proven to date one of the least satisfactory substances.

V. Valenta of Vienna, Austria, in Photographische Korrespondenz, 1910, describes a process for using asphalt, in which he claims to have eliminated many of the difficulties previously encountered, and his process is for treating asphalt with sulphur chloride, thereby converting it into a series of resins, among which he recognizes one particular substance called "gamma-resin" as being the most highly light sensitive.

Other researchers in this art have given attention to asphalt, and to asphalt compounded with certain sensitizers, but the results of their work give products which are unstable after one day and, therefore, unsatisfactory for commercial use.

As a result of numerous researches carried on by me as improvements in the Valenta process, I have found that asphalt may be converted by carbon bisulphide and sulfur chloride into a resist for photo etching, which resist is not only super-sensitive but which is perfectly practical after it has been completely prepared and stored for more than sixty days. I have, therefore, from my experiments prepared a photo etching resist which is stable over a long period of time and which has shown no sign of deterioration. Thus, I have developed an asphaltic resist which, due to its stability over a long period of time, makes it particularly adaptable and advantageous for commercial use. It is to be understood that a resist adaptable for commercial use must be one which may be satisfactorily shipped from place to place, or that may be manufactured and held in reserve for a long period of time for factory practice.

While the term asphalt has been herein used without qualification, it is to be noted that Valenta calls for a Syrian asphalt for his use. By reason of my improvements I find that I may use any asphalt or a prepared or treated asphalt. Thus, my improvements permit a much more efficiently prepared resist, and a resist which has a much wider use while at all times it is particularly adaptable for commercial use. In addition to preparing a satisfactory commercial resist from practically any grade of asphalt, I have found that my improvements permit me to substitute the asphalt by various other resins and hydrocarbons.

For the purposes of definiteness and of scientific uniformity, I prefer to consider the asphalt, its equivalents and substitutes as being hydrophobic colloids, which term is considered to refer to substances with colloidal properties, insoluble in water but soluble in an organic solvent. Valenta's asphalt and resins are to be considered as being within this term. The benzol used by Valenta is an organic solvent. In addition, the sulfur chloride employed by Valenta is a halogen agent which under certain reactions frees the halogen. The asphalt of Valenta is a natural resinous substance, and the sulfurized asphalt prepared by Valenta is a synthetic resin. All of these terms and uses, it will be seen, make the whole consideration of results of prior researchers and of my improvements definite

and of such clearness that they may all be readily understood and considered.

The numerous writers on asphalt have emphasized the desirability of using Syrian asphalt as the raw material, it apparently containing the greater proportion of light sensitive ingredients. I have found that this is not necessarily true, for by carrying out the Valenta process with the new and additional detail which is the basic discovery of this invention, practically any kind of asphalt available in the market may be used, and I have made highly satisfactory resists from ordinary Trinidad and Mexican asphalts, which resists are stable over long periods of time and which are so sensitive that they need only an exposure of 15 seconds when used with a suitable arc and condenser with an interposed light pattern carried by a glass screen.

The detail which has been added by me to the Valenta process to obtain these results will be evident when it is considered that in the Valenta process 25 grams of Syrian asphalt is dissolved in 150 cc. of carbon bisulphide to which is gradually added 2 gms. of sulfur chloride dissolved in 8 cc. of carbon bisulphide. The excess of carbon bisulphide is then distilled off and the resulting product dissolved in benzol as the solvent, and oil of lavender as the sensitizer added, and the exposed film resulting from the use of this solution being developed with turpentine. In my process, using ordinary Mexican asphalt, the sulfur chloride solution is added to the asphalt solution all at once. Practically all of the carbon bisulphide is removed by distillation after the re-action is complete, and the resulting mass dissolved in benzol. I have found that turpentine is excessively active, and instead of the pure substance, I prefer to use it in a modified form with its solvent power reduced, by the addition of a portion of petroleum benzine.

Plates of metal or other surfaces to be etched when coated with the resist thus prepared and upon which the resist is deposited in the form of a thin film, are now dipped in ether for 15 seconds before exposure to light, the ether in this short time removing from the coating those portions of the resist which are undesirable and which, if left in the film, tend to cause the film to wash away too readily after exposure by the developing solution. I have found this process of dipping the coated plate in ether for 15 seconds a further advantage in that it distinctly hardens up the film and leaves it in a condition to adhere to the metal surface very firmly. The plate after exposure is again dipped in ether, and after development to the desired degree in a mixture of 75% turpentine and 25% petroleum benzine, is then dipped in pure petroleum benzine, which has the effect of instantly stopping the further solvent action of the turpentine upon the resist so that the degree of development may be stopped at any time desired by the operator. The thus prepared plate is now baked and etched.

In carrying out my process in detail, I proceed as follows: 25 gms. of asphalt of any of the softer commercial grades available in the market, are dissolved in 150 cc. of carbon bisulphide at room temperature, and into this solution, there is immediately poured a solution of 2 grams of sulfur chloride dissolved in 8 cc. of carbon bisulphide. The mass is now warmed on the water bath until the main reaction resulting probably in the simultaneous sulfurization and chlorination of the more sensitive asphalt ingredients, has proceeded to completion, when all of the carbon bisulphide which can be readily removed at water bath temperature is distilled off. The resulting residue is now dissolved in 150 cc. benzol, the solution filtered from a small amount of insoluble matter and this solution is immediately ready for use when 2% oil of lavender is added as an accelerator and sensitizer.

From the above description, it is evident that my solution of resist is much more concentrated than that used by Valenta, who dissolved the same amount of materials in 500 cc. of benzol at the end, and I therefore obtain heavier films which are much more resistant to the action of the etching bath. While the sulfur chloride which has been added to the asphalt solution has been mainly or wholly decomposed during the re-action, it is evident, nevertheless, that since it is capable of liberating both chlorine in the free state and hydrochloric acid as the result of its action with asphalt, and also of free sulfur, any or all of these substances, as well as their products of combination may not only act as light sensitive films proper, but certain of the resulting compounds undoubtedly act as accelerators and sensitizers therefor, since oil of lavender alone, without these substances, possesses no such powerful accelerating effect.

The application of the resist as above prepared is applied to the desired surface in any known manner, and where the articles are small, preferably on a whirling table, where the volatile benzol solvent immediately evaporates. The resulting film is then dipped in ether, exposed, again dipped in ether and developed as above described. After the development, the article bearing the picture so obtained is heated on a hot plate to drive out the last portion of solvent and at the same time to in some measure sinter the film to get maximum adherence to the surface, so that at no point will it be moved from the surface by the action of the electrolyte in an electrical etching bath.

While this process as above described is particularly applicable to the production of designs by means of etching, it is evident that

either before or after etching, designs may be plated thru the resist by well known electroplating processes, and it then becomes possible to deposit the design in a metal of one color upon a metal of an entirely different color, and if the metal be first etched and subsequently plated, the surface may be left smooth, while if plated without etching, the design then appears as a superimposed or raised surface.

The main differences herein over the Valenta process as shown by the above description are that any ordinary soft asphalt which I have tried can be used; the sulfur chloride is added all at once and this results in the reaction taking a course apparently quite different from that when it is added slowly; practically all the carbon bisulphide is removed before dissolving in benzol; the amount of benzol used is decreased materially, resulting in a more concentrated resist solution; and means are provided for modifying the activity of the turpentine as a developer by reducing its solvent power by the addition of petroleum benzine. The use of ether after the application of the resist is an added detail of importance which is particularly advantageous to the process in that it purifies for photographic purposes the resist in the form of its film directly upon the surface, by its selective solvent action renders the development more accurate and uniform and in some measure increases the light sensitivity.

Inasmuch as I have found that practically any asphalt may be used, it appears that many other resins and hydrocarbons in general may be applicable to this process, for I have already obtained pictures in which this process was carried out as described except that ordinary pine rosin was used in place of asphalt, and this process, therefore, evidently has the power of converting other substances than asphalt into light sensitive films capable of being used in the etching art. Neither do I restrict this invention to the use of ether, commonly understood to be ethyl ether, as the only solvent which might be applicable to bring about the effects described, for I know that methyl ethyl ether and certain other solvents of an ethereal character are suitable substances to be used in place of ordinary ethyl ether, and in fact, I construe any organic solvent capable of removing the undesirable portion of the treated hydrophobic colloid from the light sensitive film as falling within the scope of this invention.

It is to be understood that the foregoing description of the improved resist and the process of use thereof may be varied to some extent, but such variations and changes as may be desired are considered as being within the scope of the invention as would be permitted by the broad interpretation of the following claims.

What I claim is:—

1. A photographic etching prepared by coating the object to be etched with a solution of asphalt, allowing the solvent to evaporate, washing the deposited film with ether, exposing to a light pattern, developing the image and etching.

2. A photographic etching prepared by coating the object to be etched with an artificially treated asphalt, washing in a suitable medium to increase the sensitivity of the asphalt to light, exposing to a light pattern, developing and etching.

3. A photographic etching prepared by coating the object to be etched with an artificially treated asphalt, washing in ether, exposing to a light pattern, developing and etching.

4. A photographic etching prepared by coating the object to be etched with sulfurized asphalt, washing with a suitable medium to increase the sensitivity of the coating to light, exposing to a light pattern, developing and etching.

5. A photographic etching prepared by coating the object to be etched with sulfurized asphalt, washing with ether, exposing to a light pattern, developing and etching.

6. A photographic etching prepared by coating the object to be etched with a solution of sulfurized asphalt, allowing the solvent to evaporate, washing with ether, exposing to a light pattern, developing, baking and etching.

7. A photographic etching prepared by coating the object to be etched with asphalt combined with sulfur chloride, washing with ether, exposing to a light pattern, developing and etching.

8. A photographic etching prepared by coating the object to be etched with asphalt combined with sulfur chloride and oil of lavender, washing the coating with ether, exposing to a light pattern, developing and etching.

9. As a resist for photographic etching, the benzol solution of the product of the reaction between asphalt in solution in an organic solvent and approximately 8% of its weight of sulfur chloride added to the asphalt solution all at once.

10. A supersensitive asphaltic resist for photo etching capable of resisting the action of the electrolyte in an electrical etching bath for at least thirty minutes and of being rendered insoluble by exposure to a light pattern projected thereon by means of an arc and condenser within one minute, produced by the reaction between a solution of asphalt in carbon bisulphide and sulfur chloride in carbon bisulphide, the sulfur chloride being present to the extent of approixmately 8% of the weight of the asphalt, the two solutions being mixed all at once, the reaction

product being freed from solvents at water bath temerature, and re-dissolved in benzol.

11. The method of photographic etching, including applying to a corrodible surface in film form a resist as described in claim 10, washing in ether to remove the undesirable portions, projecting a light pattern thereon, developing the pattern by means of a solvent including turpentine, baking the developed surface, and etching according to known processes.

12. A photographic medium adapted to receive a design therein by exposure to light, said medium being a thin layer placed on the object to be treated and having been subjected to the action of ether for a fraction of a minute before being subjected to light.

13. A photographic medium adapted to receive a design therein by exposure to light, said medium being a thin layer placed on the object to be treated and having been subjected to the action of ether for possibly fifteen seconds before being subjected to light.

14. A print produced by photographic process, said print being an image formed under the selective action of light in a composition including therein sulfurized asphalt and having been treated with ether before exposure.

15. A print produced by photographic process, said print being an image formed under the selective action of light in a composition of sulfurized asphalt governed by carbon bisulphide, sulfur chloride and a solvent.

16. A print produced by photographic process, said print being an image formed under the selective action of light in a composition of sulfurized asphalt governed by carbon bisulphide, sulfur chloride and benzol.

17. In the process of preparing a photographic resist having sulfur chloride therein, the step of adding at one time to a hydrophobic colloid the entire required amount of sulfur chloride.

18. In the process of preparing a resist including the reaction products of a hydrophobic colloid, sulphur chloride and carbon disulphide for photographic purposes, the step of dipping the resist after being placed on an object in a solvent of ethereal character before exposure.

19. In the process of preparing a resist for photographic purposes, the step of dipping the resist after being placed on an object in ether before exposure.

20. In the process of etching, the step of dipping the resist after being placed on an object in a solvent of ethereal character after exposure to light projected through a pattern.

21. In the process of etching, the step of dipping the resist including the reaction products of a hydrophobic colloid, sulphur chloride and carbon disulphide after being placed on an object in ether after exposure to light projected through a pattern.

22. In the process of etching, the steps of placing a resist including the reaction products of a hydrophobic colloid, sulphur chloride and carbon disulphide on an object to be etched and dipping the resist in a solution of ethereal character before exposure to light and again after exposure.

23. In the process of etching, the steps of placing a resist including the reaction products of a hydrophobic colloid, sulphur chloride and carbon disulphide on an object to be etched, and dipping the resist in ether before exposure to light and again after exposure.

24. The process of preparing a resist for photographic purposes, which process consists in adding the total required amount of sulfur chloride to a hydrophobic colloid acting as a base, adding carbon bisulphide, heating to remove a material amount of said carbon bisulphide, and dissolving the resulting mass in a suitable solvent.

25. The process of preparing a resist for photographic purposes, which process consists in adding carbon bisulphide to asphalt, adding at once all of the requirements of sulfur chloride, distilling substantially all of the carbon bisulphide from the mixture, and dissolving the resulting mass in benzol.

26. In the process of etching, the steps of providing a resist by adding carbon bisulphide to a hydrophobic colloid, adding sulfur chloride, heating to distill a material part of said carbon bisulphide, and dissolving the resulting mass in benzol; coating an article to be etched with the resist as formed, dipping the resist in ether before exposure to light, dipping the resist after exposure in a solvent of ethereal character, developing the image formed in said resist, and etching.

27. In the process of etching the steps of providing a resist by adding carbon bisulphide to a hydrophobic colloid, adding sulfur chloride, heating to distill a material part of said carbon bisulphide, and dissolving the resulting mass in benzol; coating an article to be etched with the resist as formed, dipping the resist in ether before exposure to light, dipping the resist after exposure in a solvent of ethereal character, developing, dipping the resist in a solution for arresting the developing action, and etching.

28. In the process of etching, the steps of providing a resist by adding carbon bisulphide to a hydrophobic colloid, adding sulfur chloride, heating to distill a material part of said carbon bisulphide, and dissolving the resulting mass in benzol; coating an article to be etched with the resist as formed, dipping the resist in ether before exposure to light, dipping the resist after exposure in a solvent of ethereal character, developing in

turpentine, dipping in petroleum benzine to arrest developing action, and etching.

29. The process of etching which consists in forming a resist by adding carbon bisulphide to asphalt, adding thereto the full requirement at one time of sulfur chloride, heating the resulting mass to remove a material amount of the carbon bisulphide, dissolving the resulting mass in benzol; applying the resist as formed to an article to be etched; dipping said resist as applied in ether for a friction of a minute before exposure to light, exposing the resist to a design-intercepted light; dipping the resist after exposure in ether, developing the resist in a mixture of turpentine and petroleum benzine; then dipping the resist in pure petroleum benzine to arrest the developing action; baking the resist to cause the same to adhere firmly to the object; and etching in a suitable solution.

30. The process of etching corrodible surfaces by coacting them with a hydrophobic colloid bearing constitutionally combined sulfur and chloride, removing from the film coating undesirable constituents by washing with a suitable solvent, exposing the resulting purified film to a light pattern, developing, and etching the resulting picture.

31. The process of photo etching consisting of applying to a corrodible surface a resist including the product of the reaction between asphalt and approximately 8% of its weight of sulfur chloride added thereto all at once, dissolved in carbon bisulphide as the mutual solvent and from which all excess carbon bisulphide has been removed at water bath temperature and the residue dissolved in benzol; exposing the resulting film to a light pattern, developing the pattern by means of a solution including turpentine, baking the resulting coated surface, and etching.

32. A photographic resist, including the reaction product of a hydrophobic colloid, sulphur and chlorine, and a suitable sensitizing agent, said sensitizing agent being applied to the product resulting from the combination of the colloid, sulphur and chlorine, whereby to enhance its light sensitivity.

33. A photographic medium, including the reaction product of a sulphurized asphalt composition and ether.

This specification signed this 10th day of December, 1926.

ALEX BROOKING DAVIS.

CERTIFICATE OF CORRECTION.

Patent No. 1,751,908. **Granted March 25, 1930, to**

ALEX BROOKING DAVIS.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 5, line 22, claim 30, for the word "coacting" read "coating"; and line 24, for "chloride" read "chlorine"; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 15th day of April, A. D. 1930.

M. J. Moore,
Acting Commissioner of Patents.

(Seal)