

UNITED STATES PATENT OFFICE.

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SYNTHETIC RESINS, PHOTOGRAPHIC PROCESS, AND MEDIA.

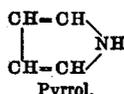
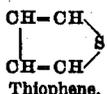
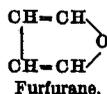
No Drawing.

Application filed November 18, 1922. Serial No. 601,827.

Our invention relates particularly to an improved photographic process, wherein synthetic resins are employed as media for producing an image, design, or character, and the invention relates further to improved media for photographic purposes.

In the practice of the invention, we utilize a class of chemical compounds for photographic purposes which hitherto has not been considered available for such purposes; a class which affords a simple medium which can be readily applied as a coating to metallic surfaces, or other surfaces, or which may be employed in any other suitable manner; a class of materials which is sensitive to the action of light to a greater or less degree, without the addition of accelerators, or sensitizers, but with which suitable sensitizers may be incorporated; a class of materials which produces a print which is readily developable with simple solvents; which affords a medium which forms an unusually good resist against the action of etching agents when the developed print is on a surface that is to be subsequently etched, for printing or other purposes; and which affords a medium depending upon its production on inexpensive materials, such as furfural, acetone, etc., whose source of supply is practically unlimited.

The principal ingredients which we use have not been classed hitherto with photographic materials. The class of compounds which has been found by us to possess remarkable adaptability to the preparation of light-sensitive media includes that group of materials containing five membered monoheterocyclic compounds, comprising the furfuran-pyrrol-thiophene group, derived from the following parent compounds. Typical examples of these compounds are here given:



It may be stated that resins, or resin-like materials, may be produced from compounds of the character referred to by known

methods, or by any approved method. For example, a resin may be produced by condensing furfural through the use of various reagents, such as aniline, hydrochloric acid, ammonia, acetone, methyl ethyl ketone, alpha-naphthylamine, sodium hydroxide, etc. While the production of resins of this general character is known and described in the literature, it has not been known hitherto that such synthetic resins can be employed advantageously in the photographic arts. The resins, or resin-like materials, produced from the compounds referred to above appear to be condensations, or polymerizations.

Our invention, in one aspect, lies in the application of one or more of these five-membered ring, heterocyclic compounds referred to above, or derivatives of the same, to photographic purposes. When, for example, such materials are applied as a film to a metallic surface, a glass surface, or other desired surface, as by flowing, spreading, or otherwise, preferably in the form of a solution of the resin having a consistency of a lacquer, or thin solution, they are so sensitive to light as to enable them to be readily utilized for photographic purposes. Photographic images may be formed readily in such media, and may be developed through the use of suitable solvents, selective dyeing, or the like.

The exact chemical reactions which bring about these radically new results are not fully known, but may, by reasonable hypothesis, be attributed to what we may designate as photo-condensation, photooxidation, photoresinification, or photo-polymerization. As heretofore stated, a furfural resin coating is in itself light sensitive to a remarkable degree without the addition of accelerators or sensitizers; yet, under certain conditions, the inclusion of sensitizers does produce acceleration.

There are many practical applications of our process, such as decorating metallic or other surfaces through the inclusion of a desired color with the coating, preparation of lithographic plates, half-tone process plates, intaglio printing plates, etc. Screenless photo litho-plates may be produced from

continuous-tone negatives because the coating becomes variably permeable to etching reagents in an inverse ratio to the light intensity of the luminous rays to which the coating has been exposed.

We have found that pyrrol and thiophene condensation products similarly produced have shown light sensitivity. These, as already stated, are alternative compounds in our process.

As examples in the practical applications of our process, we may instance the following.

(a) Furfuramide resin:

A mixture of 100 grams of furfural and 100 grams of concentrated ammonium hydroxide is introduced into a flask at room temperature. Condensation may be effected under gentle heating, if necessary. The resinous product is dried, after being separated from the entrained water, by heating to 105 degrees C. for an hour, and, when dissolved in benzene or acetone, is applied as a thin film onto the surface upon which the photographic print is to be made. Printing may be done by contact or by optical projection as desired, the time varying from one to five minutes, depending on the density of the negative, etc. After printing the image may be developed in a 25% solution of benzol (benzene) in turpentine which gives good results. The sensitivity can be increased by adding a halogen source, such as small percentages of iodoform, methyl iodide, iodine, or ammonium bichromate, so that contact prints are produced under an arc light in two and one-half minutes, instead of five, without the inclusion of a sensitizer.

Among the most sensitive substances which we have found are the furfural-ketone resins of which the following is a practical example:

(b) Furfuracetone resin:

A condensation product is produced by applying heat at about 100 degrees C. to 90 grams of furfural in 58 grams of acetone combined with 100 grams of concentrated solution of sodium hydroxide, as a condensing agent, in a reflux condenser for half an hour. The resulting product is somewhat viscous, and may be directly diluted by a suitable thinner, such as benzol, or acetone, to form a sensitive film of any desired consistency. Acetone is here given as an example of a ketone.

The condensation product may be purified and recovered by neutralizing the sodium hydroxide with acid, or acid solution, decanting, and drying the precipitate at 105 degrees C. Prints are made in the remarkably short time of ten seconds by contact printing under an arc light. Sensitizers, such as iodoform, colloidal iodide, etc., may be added if desired.

As an exemplification of photo condensa-

tion, in which furfural is used, we have found the following of practical value:

(c) Direct photo condensation:

60 grams of furfural and 40 grams of aniline are mixed, and the mixture applied directly as a thin film to a suitable surface; or, the materials are incorporated in a suitable medium, such as cellulose acetate, asphaltum, cumar resin, etc., which may in themselves be sensitive to light. When exposed to an arc light, such a mixture becomes resinous in about five minutes. In contrast to this, furfural and aniline condense only slowly without the aid of light, even when boiled together.

As another modification, the following is given:

(d) Indirect photo condensation.

The addition of small quantities of iodine in a mixture of furfural and aniline in the dark produces a viscous condensation product of a deep red color. To produce prints rapidly by means of this reaction, a mixture of furfural and aniline is sensitized by adding a small amount of iodoform, or any compound which will liberate iodine when it is exposed to light. With such a medium, accelerated reaction progresses directly upon the support which is to receive the image. A deep red coloration results under a 30 seconds exposure wherever the light has been permitted to act; and, with continuous tone negatives, the depth of color is proportional to the intensity of the light, producing a highly visible image. If desired as an etching resist on a metallic or other surface, this medium used alone or combined with another, such as cellulose acetate, may be developed by suitable solvents, like alcohol, benzol (benzene), etc.

Pyrrol product.

(e) Resinous pyrrol condensation products.

We have distilled pyrrol to purify it, and have found that the sticky resinous residue is sensitive to light, producing a print in eight minutes. After sensitization with iodoform, a print was produced in six minutes. As an alternative to this, ten grams of purified pyrrol were added to seven grams of concentrated sulphuric acid, when another resinous substance was produced. After being dried, dissolved in benzene, and applied as a film, it was found to be so light sensitive as to produce a print in two minutes.

The foregoing examples are given merely as illustrative of the invention or discovery. The invention is adaptable to a wide variety of industrial uses. Coatings, or films, produced from these media are especially resistant to the action of acids, as for etching in relief or intaglio, but more permanent in this respect than asphaltum; and the sensi-

tivity of the media is also greater than that of asphaltum.

While it is preferred to employ solutions of the synthetic resins and apply such solutions as thin coatings to suitable surfaces, the invention is not to be understood as limited to such method of use.

In our application 613,796, filed January 19, 1923, further modifications of the generic invention, herein disclosed, are set forth.

The expression "five-membered mono-heterocyclic compounds" is used herein to indicate those compounds in which one member of the ring is an element other than carbon, as for example, oxygen, nitrogen, sulphur, etc. The expression "developing the image" as used herein is intended to be broad enough to include any suitable method of treating the film, or image, subsequent to the formation of the latent image, to render the image useful for whatever purpose it is to be employed. This includes desensitizing unacted upon portions of the film, removal of unacted upon portions of the film, or vice versa, the use of mordants, dyes, etc.

The foregoing detailed description has been given for clearness of understanding only, and no unnecessary limitations should be understood therefrom, but the appended claims should be construed as broadly as permissible, in view of the prior art.

What we regard as new, and desire to secure by Letters Patent, is:

1. The process which comprises photographically forming an image, design or character which embodies a resinous product of a five-membered mono-heterocyclic compound.

2. The process which comprises applying to a metal surface a film comprising a solution of a resinous product of a five-membered mono-heterocyclic compound and photographically forming a resistant image embodying said resinous product.

3. The process of producing an image, design or character which comprises acting selectively with light upon a body comprising a resinous product of a five-membered mono-heterocyclic compound in accordance with an image, design or character, to effect the desired transformation.

4. The process of producing an image, design or character which comprises acting selectively with light upon a body comprising a resinous product of a five-membered mono-heterocyclic compound in accordance with an image, design or character, to effect the desired transformation, and developing the image.

5. The process which comprises applying to a suitable surface a coating comprising a solution of a resinous product of a five-membered mono-heterocyclic compound and acting selectively with light upon said coat-

ing in accordance with an image, design or character, to effect the desired transformation.

6. The process which comprises applying to a suitable surface a coating comprising a solution of a resinous product of a five-membered mono-heterocyclic compound and acting selectively with light upon said coating in accordance with an image, design or character, to effect the desired transformation, and developing the image.

7. The process which comprises photographically forming an image, design or character which embodies a resinous product derived from furfurals.

8. The process of producing an image, design or character which comprises acting selectively with light upon a body comprising a resinous product derived from furfurals in accordance with an image, design or character, to effect the desired transformation.

9. The process of producing an image, design or character which comprises acting selectively with light upon a body comprising a resinous product derived from furfurals, in accordance with an image, design or character, to effect the desired transformation, and developing the image.

10. The process which comprises applying to a desired surface a solution of a resin derived from the furfurals, acting selectively with light upon the film thus produced upon said surface, in accordance with an image, design or character, to effect the desired transformation, and developing the image.

11. The process which comprises photographically forming an image, design or character which embodies a condensation product of a furfural and a ketone.

12. The process which comprises forming an image, design or character by acting selectively with light upon a body comprising a condensation product of a furfural and a ketone in accordance with an image, design or character, to effect the desired transformation.

13. The process which comprises forming an image, design or character by acting selectively with light upon a body comprising a condensation product of a furfural and a ketone in accordance with an image, design or character, to effect the desired transformation, and developing the image.

14. The process which comprises applying to a suitable surface a solution of a condensation product of a furfural and a ketone to form a film on said surface, and acting selectively with light upon said film in accordance with an image, design or character, to effect the desired transformation.

15. The process which comprises applying to a suitable surface a solution of a condensation product of a furfural and a ketone to form a film on said surface, acting selec-

tively with light upon said film in accordance with an image, design or character, to effect the desired transformation, and developing the image.

- 5 16. The process which comprises photographically forming an image, design or character which embodies a condensation product of a furfural and ethyl methyl ketone.
- 10 17. The process of producing an image, design or character which comprises acting selectively with light upon a body comprising a condensation product of a furfural and ethyl methyl ketone in accordance with
- 15 an image, design or character to effect the desired transformation.
18. The process of producing an image, design or character which comprises acting selectively with light upon a body comprising
- 20 a condensation product of a furfural and ethyl methyl ketone in accordance with an image, design or character to effect the desired transformation, and developing the image.
- 25 19. The process which comprises applying to a suitable surface a film comprising a solution of a condensation product of a furfural and ethyl methyl ketone, acting selectively with light upon said film in accordance with an image, design or character to
- 30 effect the desired transformation, and developing the image.
20. The process which comprises photographically forming an image, design or
- 35 character which embodies a resinous product of a five-membered mono-heterocyclic compound having incorporated therewith a sensitizer.
21. The process of producing an image,
- 40 design or character which comprises acting selectively with light upon a body comprising a resinous product of a five-membered mono-heterocyclic compound and a sensitizer incorporated therewith, in accordance with
- 45 an image, design or character, to effect the desired transformation.
22. The process which comprises applying to a suitable surface a film comprising a solution of a resinous product of a five-membered mono-heterocyclic substance having
- 50 incorporated therewith a sensitizer, and acting selectively with light upon said film in accordance with an image, design or character, to effect the desired transformation.
- 55 23. The process which comprises photographically forming an image, design or character which embodies a condensation product of a furfural and a ketone, having incorporated therewith a sensitizer.
- 60 24. The process of producing an image, design or character which comprises acting selectively with light upon a body comprising a condensation product of a furfural and a ketone associated with a small percentage of a sensitizer, in accordance with
- an image, design or character, to effect the desired transformation.
25. The process which comprises applying to a suitable surface a film comprising a
- 70 solution of a condensation product of a furfural and a ketone associated with a small percentage of a sensitizer, acting selectively with light upon said film in accordance with an image, design or character, to effect the desired transformation, and developing the
- 75 image.
26. The process of producing an image, design or character which comprises acting selectively with light upon a body comprising a resinous product of a five-membered
- 80 mono-heterocyclic compound, associated with a sensitizer comprising a halogen source, in accordance with an image, design or character, to effect the desired transformation.
27. The process of producing an image,
- 85 design or character which comprises acting selectively with light upon a body comprising a condensation product of a furfural and a ketone, associated with a sensitizer comprising a halogen source, in accordance with
- 90 an image, design or character, to effect the desired transformation.
28. A photographic medium comprising a resinous material derived from a five-membered mono-heterocyclic compound, associated
- 95 with a sensitizer.
29. A photographic medium comprising a resinous material derived from a five-membered mono-heterocyclic compound, associated with a sensitizer comprising a halogen
- 100 source.
30. A photographic medium comprising a resinous material derived from a five-membered mono-heterocyclic compound, associated with a sensitizer and a solvent.
- 105 31. A photographic medium comprising a condensation product of a furfural and a ketone, associated with a sensitizer.
32. A photographic medium comprising a condensation product of a furfural and a
- 110 ketone, associated with a sensitizer comprising a halogen source.
33. A photographic medium comprising a condensation product of a furfural and a ketone, associated with a sensitizer, and a
- 115 solvent in which said materials are dispersed.
34. A photographic print comprising an image formed in accordance with the selective action of light in a body comprising a resinous material derived from a five-membered mono-heterocyclic compound.
- 120 35. A photographic print comprising an image formed in accordance with the selective action of light in a body comprising a condensation product of a furfural.
- 125 36. A photographic print comprising an image formed in accordance with the selec-

tive action of light in a body comprising a condensation product of a furfural and a ketone.

suitable foundation, and a film thereon comprising a condensation product of a furfural and a ketone.

37. A photographic print comprising an image formed in accordance with the selective action of light in a body comprising a condensation product of a furfural and an ethyl methyl ketone.

41. A photographic plate comprising a suitable foundation, and a film thereon comprising a condensation product of a furfural and ethyl methyl ketone.

38. Means for receiving photographic impressions, comprising a suitable foundation and a film thereon comprising a resinous product derived from a monoheteratomic five-membered ring compound.

42. A photographic plate comprising a suitable foundation, and a film thereon comprising a condensation product of a furfural and a sensitizer associated with said condensation product.

In testimony whereof we affix our signatures.

39. A photographic plate comprising a suitable foundation, and a film thereon comprising a condensation product of furfural.

40. A photographic plate comprising a

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