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SYNTHETIC RESINS, PHOTOGRAPHIC PROCESS, PHOTOGRAPHIC MEDIA, AND METHOD OF PREPARING SAME.

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The present invention relates to the employment of synthetic resins in photographic processes, to photographic media, and to methods of preparing the same.

The primary object is to render available for photographic purposes a class of materials which has not hitherto been known to be available for such purposes.

In accordance with the present invention or discovery, a suitable photographic medium comprising a synthetic resin, or synthetic resins, is prepared; and use is made of such medium for various photographic purposes.

Various kinds of synthetic resins are known, or may be produced. All these resins, apparently, are light-sensitive in some degree, but some of them are very much more light-sensitive than others. In general, it is desirable to associate with synthetic resins a suitable sensitizing agent which will serve to expedite the transformation of the resin under the selective action of light. However, in some instances, it is quite feasible to omit the use of a special sensitizing agent, and still secure the transformation within a reasonably short period of time.

The present invention pertains broadly to the use of synthetic resins for photographic purposes. In our application No. 601,827, filed November 18, 1922, is described and claimed that species of the present invention which relates to the use of five-membered mono-heterocyclic compounds for photographic purposes; in our application No. 603,115, filed November 24, 1922, is described and claimed another modification of the present invention, which pertains to the use in photographic processes of phenolic condensation products; and in our application No. 613,796, filed January 19, 1923, is set forth and claimed another species of the present invention, which pertains more particularly to the use of synthetic resins produced from the five-membered mono-heterocyclic compounds and amine bodies, with a stated preference for a synthetic resin produced by condensing furfural with B-naphthylamine.

A synthetic resin, associated with a sensitizing agent, or with such sensitizing agent omitted, depending upon the degree of natural sensitiveness of the resin, or depending upon the particular results desired, may, in accordance with the present invention, be subjected to the selective action of light in accordance with an image, design or character, and thus there may be produced in the sensitive body, or film, a transformation, resulting in an image, design or character in such body, or film; and the film, or image, may then be developed in any suitable manner.

In general, it is preferred to employ a solution of a synthetic resin, capable of producing a film, or coating, on a suitable support or surface; and with many of the different kinds of resins, it is advisable to employ special sensitizers, and preferably a sensitizer which comprises a halogen source, or a halogen-liberating compound.

In carrying out the invention, use may be made of various known synthetic resins, among which may be mentioned resins, or resinous substances, derived from the five-membered mono-heterocyclic compounds referred to in our application No. 601,827, mentioned above; the phenolic condensation products referred to in our application No. 603,115, mentioned above; and other synthetic resins, or resinous compounds, mentioned in our various pending applications. In any case, it is desirable to produce an initial or incipient condensation, and thus provide a synthetic resinous body which is capable of being dissolved in suitable solvents and which is capable of being further transformed selectively under the action of light; and, where necessary to associate with the condensation product a suitable sensitizer which will perform the function of accelerating the transformation under the selective action of light. As indicated above, use may be made of synthetic resins produced in accordance with well known methods. It may be added that extended researches have been made by us with various classes of organic compounds, which, when mixed together at room temperature, or slightly above, have condensed to form viscous polymerization products. Such condensations may be accelerated by the presence of various ingredients, such as iodine, or other halogen. We have found that com-

pounds of a halogen, such as iodoform, or the metal alkyl halides, liberate halogen under the action of light. Such sensitizers may be used advantageously in connection with most of the synthetic resins to continue by photo polymerization, halogenation, or catalytic action, the selective condensation.

The following examples may be given by way of illustration:

(1) Mix together 35 grams of dimethyl aniline, 14 grams of benzaldehyde, and 4 grams of iodine; and allow the mixture to stand at room temperature for about three days. There results a viscous green product. Through the addition of 1 gram of iodoform to 10 grams of the resin, there is produced a sensitive coating, which gives a print in about two minutes by optical projection in the usual manner.

(2) Mix 15 grams of phenol, 15 grams 40% formaldehyde solution and 1 gram iodine; allow the same to stand at room temperature about forty-eight hours. This results in a resinous condensation product. 10 grams of this resin dissolved in 50 cc. of butyl acetate with 3 grams of iodoform added, produces a sensitive coating, which gives a print in about three minutes. This is developable, for example, in 75% alcohol.

(3) Mix together 4 grams of iodine, 10 grams benzaldehyde, 18 grams aniline; allow this mixture to stand overnight. This results in a viscous product, soluble in acetone. Mix 10 grams of this resin with 50 grams of acetone and 3 grams of iodoform. This produces a solution affording a coating which enables a print to be produced with an exposure of forty-five seconds.

(4) Mix 18 grams of aniline, 10 grams 40% formaldehyde and 2 grams iodine. Quite a rapid reaction results at room temperature, resulting in the formation of a yellowish green viscous substance. Mix 10 grams of this initial condensation product with 50 grams of acetone and 3 grams iodoform. This provides a solution which may be applied as a coating to a suitable surface, and the continuing condensation, or transformation, may be completed satisfactorily by an exposure of forty-five seconds.

(5) Mix 18 grams of benzyl aniline, 4 cc. of 40% formaldehyde solution, 2 cc. of water, and a drop of concentrated hydrochloric acid; heat in a reflux condenser for an hour, thus producing a synthetic resin. 4 grams of this resin dissolved in 30 grams benzol (benzene) and 1 gram iodoform gives a solution, which, in the form of a film, yields a print in thirty seconds. This print may be developed with benzine and turpentine.

(6) Mix 100 grams benzyl chloride, 1 gram of powdered ferric chloride and 3 cc. of concentrated sulphuric acid; heat the mixture for about an hour under a reflux condenser, or until it forms a solid resinous mass. Dissolve 4 grams of this resin in 30 cc. of benzol, to which 1 gram of iodoform is added. This solution will give a dry coating on which prints may be made by contact, completing the continuing condensation, or necessary transformation. in about thirty seconds. Such prints are developable in a mixture of 50 parts of benzine and 50 parts of turpentine.

Reference has already been made to phenolic condensation products. As is well known, such condensation products can be formed by condensing the phenols with active methylene bodies, such as formaldehyde, hexamethylenetetramine, or other active methylene body. Resins thus produced can be readily sensitized by means of a small percentage of iodoform, as in the example of the phenolic condensation product given above. Other sensitizing agents may be employed.

Reference also has been made to our pending application No. 601,827, describing the use of condensation products derived from the five-membered mono-heterocyclic compounds, preferably furfural. As was pointed out in said application, some of these furfural resins particularly are very sensitive to light, and may be usefully employed without associating therewith any special sensitizer. In some of the resins of the type just referred to, however, it is advisable to employ special sensitizers, such as sensitizers comprising a halogen source, or a halogen-liberating compound.

It will be understood from the description thus far given that it is desirable, or necessary, to use only small percentages of a sensitizing agent, or sensitizing agents, where the use of a special sensitizer is required. In all cases, the preliminary condensation is carried far enough to give a suitable resinous body which can, where desired, be placed in solution; and the subsequent condensation is carried on, or effected under the selective action of light, either by contact printing, or by projection, in accordance with an image, design or character. This results in the formation of an image, design or character in the resinous body which differs in solubility, or in a degree of solubility, from those portions of the resin which are not acted upon by the light; and the image may then be developed, or fixed, in accordance with known methods, or any suitable method. Where a halogen-liberating compound is employed as a sensitizing agent, the halogen is liberated under the action of light, and doubtless, serves as a catalyzing agent, expediting the further reaction which occurs under the action of light. Thus, there is produced under the action of light a continuation of the condensation, forming areas of variable and selective solubility, in accordance with the va-

riable luminous characteristics of the image through which the light is transmitted, or projected.

From the examples given, it will be understood that iodine has the property of greatly promoting condensations in synthetic resins. Iodoform is very desirable as an accelerating, or sensitizing, agent; and, as indicated above, the metal halides may be used advantageously. The sensitizing agent employed may comprise one or more of any suitable sensitizers. While iodine has been specifically mentioned as a halogen for use in the process, other halogens, such as chlorine, or bromine, may be used, or halogen-liberating compounds comprising these materials may be used.

A useful method of employing the invention is that of covering a suitable surface with a light-sensitive coating; and exposing the same to a luminous image, by optical projection, or by contact printing. In general, the methods known in the art may be followed. After the prints have been formed, they may be developed in any suitable manner. Any solvent that will react on the parts of the coating which have not been acted upon by light, or vice versa, may be used, as desired. In short, any suitable method of developing, or fixing, the print, or image, may be employed.

As has been indicated, the preliminary condensation may be brought about in any suitable manner, as by heat, the use of condensing reagents, or by preliminary exposure to light in the presence of a catalyst; and the subsequent transformation may be effected either in the presence of a special sensitizer, or without such special sensitizer, depending upon the effects desired.

Suitable resinous compounds are produced by combining a wide variety of substances, those referred to above being given as examples. It is immaterial whether the preliminary condensation is initiated or effected by a halogen, or in any other manner. It may be stated that most of the condensation reactions are accelerated by the addition of a halogen, particularly under the action of light.

Even though we have predicated our invention on the preliminary condensation effect and a further continuing condensation produced by the selective action of light, we do not exclude those materials which operate practically in the same manner, even though the initial product formed may not be technically regarded as a preliminary condensation product. For example, some of the furfural resins, in their initial stages, may be regarded by some as not being true synthetic resins, but rather as being in the nature of addition products. In any case, however, for the purpose of the present invention, these initial products act like preliminary condensations. That is to say, the further, or final, condensation is quickly and selectively accomplished by the action of light as transmitted, or projected, through an image, design or character.

While it is preferred to employ these light-sensitive bodies in the form of varnishes or lacquers, it is to be borne in mind that the bodies themselves possess the capability of transformation under the action of light. Hence, we do not limit ourselves to the use of such bodies in solution.

Various uses to which the invention may be put will occur to those skilled in the art of photographic processes as employed in the industrial arts, and specific enumeration of the same herein is unnecessary.

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.

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

1. A photographic process comprising: preliminarily forming a synthetic resinous compound which is capable of condensation under the action of light; and subjecting the same to the selective action of light in accordance with a luminous image to effect the desired transformation.

2. A photographic process comprising: preliminarily forming a synthetic resinous compound which is capable of condensation under the action of light; subjecting the same to the selective action of light in accordance with a luminous image to effect the desired transformation; and developing the image.

3. A photographic process comprising: forming a coating comprising a solution of a synthetic resinous compound susceptible of being condensed under the action of light; and subjecting said coating to the selective action of light in accordance with a luminous image to effect selective condensation.

4. A photographic process comprising: forming a coating comprising a solution of a synthetic resinous compound susceptible of being condensed under the action of light; and subjecting said coating to the selective action of light in accordance with a luminous image to effect selective condensation; and subjecting the print to a developing operation.

5. The process which comprises: subjecting a body comprising a synthetic resin, capable of being transformed under the action of light, to the selective action of light in accordance with a luminous image until the desired transformation is effected.

6. The process which comprises: subjecting a body comprising a synthetic resin capable of being transformed under the action

of light to the selective action of light in accordance with a luminous image until the desired transformation is effected, and developing the print.

7. A photographic process which comprises: subjecting to the selective action of light in accordance with a luminous image a body comprising a synthetic resin and an associated sentitizing agent.

8. A photographic process which comprises: subjecting to the selective action of light in accordance with a luminous image a body comprising a synthetic resin and an associated sensitizing agent comprising a halogen source.

9. A photographic process which comprises: subjecting to the selective action of light in accordance with a luminous image a body comprising a synthetic resin and an associated sensitizing agent comprising a halogen-liberating compound.

10. A photographic process which comprises: subjecting to the selective action of light in accordance with a luminous image a body comprising a synthetic resin and an associated sensitizing agent comprising a halogen-substituted hydrocarbon.

11. A photographic process which comprises: subjecting to the selective action of light in accordance with a luminous image a body comprising a synthetic resin and an associated sensitizing agent comprising iodoform.

12. A photographic process which comprises: subjecting to the selective action of light in accordance with a luminous image a body comprising a synthetic resin and an associated sensitizing agent comprising a halogen-substituted hydrocarbon and a metallic halide.

13. A photographic process which comprises: applying to a surface a coating comprising an artificial resinous compound capable of being condensed under the action of light, such compound having associated therewith a sensitizing agent; and subjecting said coating to the selective action of light in accordance with a luminous image and thereby selectively changing the coating into variable condensation areas.

14. A photographic process which comprises: applying to a surface a coating comprising an artificial resinous compound capable of being condensed under the action of light, such compound having associated therewith a sensitizing agent; subjecting said coating to the selective action of light in accordance with a luminous image and thereby selectively changing the coating into variable condensation areas; and developing the coating.

15. A photographic process which comprises: applying to a surface a coating comprising a solution of a synthetic resin and sensitizing agent; and effecting transformation of said coating selectively by acting thereon with light in accordance with a luminous image.

16. A photographic process which comprises: applying to a surface a coating comprising a solution of a preliminary condensation product and an associated sensitizing agent; and selectively transforming said coating by the action of light in accordance with a luminous image.

17. A photographic process which comprises: applying to a surface a coating comprising a solution of a preliminary condensation product and an associated sensitizing agent; selectively transforming said coating by the action of light in accordance with a luminous image; and developing the coating.

18. A photographic process which comprises: applying to a surface a coating comprising a solution of a resinous compound capable of being condensed under the action of light, such compound having associated therewith a sensitizing agent comprising a halogen source; and acting on said coating selectively with light in accordance with a luminous image.

19. A photographic process which comprises: applying to a surface a coating comprising a solution of a resinous compound capable of being condensed under the action of light, such compound having associated therewith a sensitizing agent comprising a halogen-liberating compound; and acting on said coating selectively with light in accordance with a luminous image.

20. A process which comprises: subjecting to the selective action of light in accordance with a luminous image a body comprising a resinous condensation product of benzaldehyde.

21. A process which comprises: subjecting to the selective action of light in accordance with a luminous image a body comprising a resinous condensation product of benzaldehyde and aniline.

22. A process which comprises: subjecting to the selective action of light in accordance with a luminous image a body comprising a condensation product of benzaldehyde, associated with a halogen-liberating agent.

23. The process of producing a photographic medium which comprises incorporating with a synthetic resin compound capable of being condensed under the action of light a sensitizing agent adapted to accelerate the action of light in a photographic action.

24. The process of producing a photographic medium which comprises incorporating with a preliminary condensation product a sensitizing agent.

25. The process of forming a photographic medium which comprises incorporating with a preliminary condensation product which is capable of further con-

densation under the action of light a sensitizing agent comprising a halogen source.

26. The process of forming a photographic medium which comprises incorporating with a preliminary condensation product which is capable of further condensation under the action of light a sensitizing agent comprising a halogen-liberating compound.

27. The process of forming a photographic medium which comprises incorporating with a preliminary condensation product which is capable of further condensation under the action of light a sensitizing agent comprising a halogen-substituted hydrocarbon.

28. The process of forming a photographic medium which comprises incorporating with a preliminary condensation product which is capable of further condensation under the action of light a sensitizing agent comprising iodoform.

29. A photographic medium comprising a synthetic resin compound capable of being condensed under the action of light, and a sensitizing agent incorporated therewith adapted to accelerate the action of light under photographic action.

30. A photographic medium comprising a resin compound capable of being condensed under the action of light, and a sensitizing agent incorporated therewith comprising a halogen-liberating compound.

31. A photographic medium comprising a resin compound capable of being condensed under the action of light, and a sensitizing agent incorporated therewith comprising a halogen-substituted hydrocarbon.

32. A photographic medium comprising a resin compound capable of being condensed under the action of light, and a sensitizing agent incorporated therewith comprising iodoform.

33. A photographic medium comprising a solution of a resin compound capable of being condensed under the action of light, associated with a sensitizing agent.

34. A photographic medium comprising a solution of a resin compound capable of being condensed under the action of light, associated with a sensitizing agent comprising a halogen-liberating compound.

35. A photographic medium comprising a solution of a resin compound capable of being condensed under the action of light, associated with a sensitizing agent comprising iodoform.

36. A print comprising a synthetic resin embodying a photographically formed image, design or character.

37. A print comprising a condensation product of benzaldehyde embodying a photographically formed image, design or character.

In testimony whereof we affix our signatures.

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