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

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The present invention relates to synthetic resins photographic process, media and method of preparing same.

The invention constitutes a species of the generic invention pertaining to the use, for photographic purposes, of condensation products derived from the monoheteratomic five-membered ring compounds, set forth in our pending application No. 601,827, filed November 18, 1922; and the application just referred to constitutes, in turn, a species of the generic invention set forth and claimed in our application No. 613,795, filed January 17, 1923.

The purpose of the present invention is to provide for the use, for photographic purposes, of a medium, which, comparatively speaking, is very rapid in the transformation which occurs under the action of light transmitted to, or projected upon, the medium in accordance with a luminous image.

In the present invention, we make use principally of condensation products, or resins, derived from a five-membered monoheterocyclic compound, preferably furfural, and an amine body; and the amine body which it is preferred to employ in obtaining the resin which is to be embodied in the photographic medium preferably is B-naphthylamine. It has been found possible, in accordance with the preferred steps disclosed herein, to produce a photographic medium which is several times more rapid than the furfural-acetone process, as practiced by us prior to November 18, 1922 and as described in application No. 601,827.

In our application 601,827, reference is made to numerous reagents which may be combined with furfural, for example, to produce resinous substances. The reagents there mentioned include some of the amines, such as ammonia, alpha-napthylamine, and aniline.

The present invention utilizes ingredients which, in some instances, appear to be addition products, as distinguished from actual preliminary condensation products. Nevertheless, these addition products, if such they be, are found to be in suitable physical form to enable them to be used in a photographic medium, and are in suitable condition to enable them to be readily transformed under the selective action of light in accordance with a luminous image, design or character.

While the use of the product derived from B-naphthylamine and furfural is preferred, numerous other examples are set forth herein of resins derived from furfural and amine bodies which may be regarded as practical equivalents for the purposes of the present invention.

For the purpose of enabling the invention to be understood and ascertained. the following description is given, setting forth various exemplifications:

While, in general, resins derived from furfural are quite light-sensitive, nevertheless, it may be useful to employ sensitizers in conjunction with these resins, or some of them. It has been found to be the case, particularly in the resins derived from furfural and the amine bodies, that the use of sensitizers is desirable. Various sensitizers may be employed. Preferably the sensitizer will comprise a halogen source, or a halogen-liberating compound. A halogen-substituted hydrocarbon, such as iodoform, affords a very desirable sensitizer. Such sensitizers serve to accelerate the transformation which occurs under the selective action of light transmitted, or projected, upon the sensitive body in accordance with a luminous image, design or character. Halogen is liberated under the action of light and, doubtless, acts as a catalyzer, hastening the reaction.

We have found that in this B-naphthylamine furfural process a mixture of the two ingredients indicate no condensation at room temperature, and yet the mixture is in suitable physical condition to use as a coating in which the actual condensation will practically not take place until iodine is liberated from a sensitizer, such as iodoform. When the iodine constituent is liberated by light, the coating condenses

rapidly forming an exceedingly rapid printing medium. If B-naphthylamine and furfural are mixed together, they form a solid substance inside of a few minutes that has a resinous appearance, but cannot, perhaps, be strictly classified as a resin until this state is reached after condensation has taken place under the action of light.

We have found that two parts of B-naphthylamine and one part of furfural mixed together react very rapidly at room temperature to form a resin-like material readily soluble in benzol. 20 grams of the mixture dissolved in 100 cc. of benzol forms a solution, from which 20 grams added to one gram of iodoform produced a light-sensitive coating which gave prints in from one-fifth to one-tenth of the time required for a furfural acetone coating, and the prints are developed with great facility in turpentine or alcohol and water. In contrast to the furfural acetone process, iodoform in this case is a rapid sensitizer. This sensitization is so marked that we have found it exceedingly difficult to get any kind of print without the use of the iodoform.

Without limiting ourselves to a disclosure of the ultimately exact chemical reactions, it appears that the first action in combining B-naphthylamine and furfural is a solvation step, even though the product is solid and has a resinous appearance, because the B-naphthylamine can still be dissolved out of the mixture by water which is not the case after condensation has actually occurred. In other words, it is believed that furfural and B-naphthylamine form an unstable addition product when mixed and really only condense under the influence of iodine and the action of light. It may also be said that the B-naphthylamine crystals when mixed into the furfural immediately go into solution fairly completely at room temperature, and that no actual condensation takes place until the temperature is increased to near 100 degrees C., or unless free iodine or a halogen catalyzer be added. The iodoform under the action of light liberates iodine which immediately starts real condensation with great rapidity. This speed is probably dependent practically upon the rate at which the iodine is liberated from the iodoform, indicating that additional speed in printing action may be dependent more or less on the catalyzing liberation of iodine from iodoform by light.

Equimolecular proportions of furfural and B-naphthylamine work as well as the proportions noted above. We have also found that there are other combinations which give practical results as follows:

15 parts of B-naphthylamine and 10 parts of furfural are mixed to form a solid mass at room temperature. Enough of this is dissolved in naphtha to make about a 23 per-cent solution. To 50 grams of the above solution, 5 grams of iodoform and ½ cc. of eugenol is added. This forms a coating that prints in thirty seconds and which is developed in benzine and not in benzol.

We have found the following modifications of the eugenol procedure to produce contact prints in ten seconds which are developable in turpentine. 65 grams of the furfural B-naphthylamine compound is heated to 175 degrees C., for twenty minutes, and then diluted with 500 cc. of solvent naphtha, and filtered. A portion remains insoluble in the solvent naphtha but it can be dissolved in ethyl methyl ketone, and it is quite insensitive to light. To 50 grams of the solvent naphtha solution, 2 grams of iodoform and 1 gram of eugenol are added to form a coating which contains approximately 10 per cent of the resin.

We have also determined the relative value of ammonium bichromate as a sensitizer and have found that it accelerates the condensation under the action of light very slightly, being less reactive than iodine, indicating a sensitivity that is but very little more than that of the resin itself, which requires about ten minutes to obtain a very poor print.

When furfural and aniline are mixed at room temperature, they react to form a yellow precipitate combined with some water given off by the reaction. By dehydrating this precipitate with a substance such as calcium chloride, the water is eliminated and a sticky mass remains which is an addition product analogous to that obtained by the interaction of furfural and B-naphthylamine. Such an addition product dissolves in benzol, and, when sensitized by means of iodoform, produces a light sensitive coating on which prints are produced in less than a minute.

Benzaldehyde has come to be considered somewhat analogous to furfural in most of its reactions, although it belongs to a different group of organic compounds. 10 grams of this substance and 20 grams of B-naphthylamine when mixed at room temperature also form an addition product that is solid and resembles that formed by furfural and B-naphthylamine. Such a product combined with a benzol solvent and sensitized with iodoform prints in a very similar though somewhat slower manner.

Formaldehyde and B-naphthylamine mixed at room temperature form a white precipitate addition product which resembles the previous exemplifications. We formed a coating mixture by taking 20 grams of B-naphthylamine and 30 grams of formalin solution and made a 20 percent solution in acetone. 20 cc. of this mixture was sensitized with 2 grams of iodoform, producing good prints in fifteen seconds.

The various exemplifications of printing

time, etc., all relate to similar illuminating conditions. The printing of an image, whether by contact or by optical projection, is so well understood in the art that the same is not described.

We have also found that a mixture of two substances, forming an additional product, when free iodine is added, under the action of light, condenses to a resin proportional to the varying intensity of the light. This is exemplified as follows: An addition product of furfural-B-naphthylamine is a pinkish appearing solid substance. If this is heated, it condenses to a dark brown resin which was not expected to print as rapidly as the addition product. By itself it is not sensitive, but by the addition of a little iodoform it is fully as sensitive as the other compounds. This step has been exemplified in the eugenol adaptation above. From this it is believed that the reaction in all of these exemplifications is simply the formation of condensation products of the synthetic resin by the halogen under the action of light. Some compounds print faster than others and an explanation of this variableness to light action has not as yet been found, but many of those described and probably numerous other related compounds are rapid enough to form commercially available processes.

Our light-sensitive mixtures may be applied to the desired surfaces as a coating in any well known manner by flowing, brushing, whirling, etc. Since these steps in and of themselves do not constitute a part of this invention, they are not described in detail, and we do not confine or limit ourselves to any of these or other expedients.

In addition to the previous B-naphthylamine-furfural exemplications, we have also found that the following adaptations of other ingredients produce light-sensitive mixtures which have been used to produce prints under similar lighting conditions as in the previous exemplifications in the times indicated under each exemplification.

When 19.6 grams of cyclohexanone and 38.4 grams of furfural are combined with 15 grams of a 50% caustic soda solution and heated in a reflux condenser, a resinous substance is formed which is soluble in ethyl methyl ketone. Dissolving enough of the resinous substance in the solvent to make a 10% solution produces a mixture that, when applied to a surface as a coating, will produce a print by contact, without a sensitizer in approximately four minutes. When sensitized with 1½ grams of iodoform, prints are produced under similar lighting conditions in 2½ minutes.

In another exemplification, 25 grams of metatoluylenediamine (technical) and 45 grams of furfural are mixed at room temperature and are allowed to stand about twelve hours to form a hard and brittle resin. A 20% solution of the resin in benzol, after standing about one-half hour, forms a light-sensitive mixture, which, through the addition of one gram of iodoform to 20 cc. of such solution, is printable in from 10 to 30 seconds, and is developed in a 50—50 benzol-benzine solvent. The resin, without the addition of a sensitizer, under the same exposure, etc., produces a similar print in about four minutes.

A para-toluidine-furfural adaptation is carried out by heating 20 grams of para-toluidine and 10 grams of furfural on a hot plate for 2½ hours to a temperature of about 150 degrees C. This produces a hard dark brown resin. A 20% solution of this is made in acetone, and 20 cc. of this solution, when sensitized with 1 gram of iodoform, prints in about three minutes, and is also developed in 50—50 benzol-benzine.

We have also combined 20 grams of benzidine and 20 grams of furfural at room temperature to form a resinous mass. A 20% solution was made in ethyl methyl ketone and 20 cc. of this solution was sensitized with 1 gram of iodoform, producing a mixture that gave prints in from three to ten seconds that were also developed as in the preceding exemplification.

A hard brittle resin is formed in 2½ to 3 hours at room temperature through the reaction of 25 grams each of metaphenylenediamine (technical) and furfural. 20 cc. of a 20% solution of the resin in acetone, sensitized by 1 gram of iodoform, prints in from 5 to 20 seconds. These prints are developed in 80 parts of benzol and 20 parts of benzine.

We have also combined xylidine (technical) and furfural. The reaction of 25 grams of each is similar to that of aniline and furfural. 10 cc. of the mixture in 2 cc. of benzol and ½ gram of iodoform produces a light-sensitive mixture that prints by projection in 30 to 60 seconds. When a single drop of a 9% solution of idodine in benzol is added to xylidine-furfural mixture, there results a thick viscous mass in about 48 hours. 20 grams of this, when sensitized with 1 gram of iodoform and thinned with 15 cc. of benzol, will form a coating that prints in 30 seconds and which may be developed in turpentine.

We have produced a light-sensitive mixture that without the use of a sensitizer produces prints similar to our furfural-acetone coatings, heretofore referred to, in from 30 seconds to 3 minutes, depending upon the character of the negative and the metal upon which it is printed, the lighting conditions being similar to other exemplifications referred to above. This alternative or equivalent resin was formed by mixing 10 grams of mesityloxide and 30 grams of furfural with 5 grams of a 10% solution

of caustic soda in a reflux condenser under gentle heat. After neutralization with hydrochloric acid, the resulting resin was baked at 115 degrees C. for 5 hours, after which 20 grams of the resin were dissolved in 100 cc. of benzol to form the light-sensitive coating. Prints may be developed in 50—50 turpentine and benzol. The light sensitivity of the above mixture is increased only slightly through the addition of iodoform.

In addition to the previously described exemplifications, we have found that cyclohexane-carboxylic and furfural act similarly to cyclohexanone and furfural. In any of these exemplifications, we do not limit ourselves to the use of special developing agents where such are specifically mentioned. In other cases, where no developing agent is referred to, any suitable cooperating developer may be employed, such as halogen-liberating agents, etc.

In our use of furfural acetone and mesityl-oxide furfural coatings, we have found present in developed prints a very delicate crackling effect formed in the coating in a selective manner, being quite analogous to the early forms of aquatint ground and more remotely similar to gelatinous reticulation. These delicate irregularly formed cracks expose the bare metal to the action of whatever mordant may be used, and they appear to lend themselves specially to the production of photo or rotogravures.

It is not improbable that the effect of the light on our sensitive coating is such that the sensitizer sets free variable quantities of catalyst so as to cause selective condensation of the addition compounds and thereby reproduce the image which has been projected on the coating in an optical manner through space or in contact therewith.

While it is preferred to employ solutions of the resins, so that such solutions can be readily applied as a coating to any suitable surfaces, the invention is not to be understood as limited in this respect. As will readily occur to those skilled in the art of photographic processes as employed for industrial purposes, the present invention may be put to many different useful applications.

It will be understood, of course, that the film, or image, may be developed, or fixed, in any suitable manner.

In our pending application No. 601,827, filed November 18, 1922, reference is made to the use of A-naphthylamine in connection with furfural to produce a resin suitable for photographic purposes. The B-naphthylamine furfural-resin is, however, more rapid in its action, and is preferred. In our application No. 613,795, filed January 19, 1923, reference is made to the use of other amine bodies, for example, dimethyl-aniline and benzyl-aniline. Such bodies may be employed within the scope of the present invention.

Also, in our application No. 601,827, it is pointed out that furfural is included with pyrrol and thiophene in a class, or group of substances, constituting five-membered mono-heterocyclic compounds. These substances are to be regarded as equivalents, in the broad sense.

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 which comprises: acting selectively with light in accordance with an image, design or character upon a resinous compound derived from an amine and a five-membered mono-heterocyclic compound.

2. A photographic process which comprises: acting selectively with light in accordance with an image, design or character upon a resinous compound derived from an amine and a five-membered mono-heterocyclic compound, and developing the print.

3. A photographic process which comprises: acting selectively with light in accordance with an image, design or character upon a resinous compound derived from an amine and furfural.

4. A photographic process which comprises: acting selectively with light in accordance with an image, design or character upon a resinous compound derived from an amine and furfural, and developing the print.

5. A photographic process which comprises: acting selectively with light in accordance with an image, design or character upon a resinous compound derived from naphthylamine and a five-membered mono-heterocyclic compound.

6. A photographic process which comprises: acting selectively with light in accordance with an image, design or character upon a resinous compound derived from B-naphthylamine and a five-membered mono-heterocyclic compound.

7. A photographic process which comprises: acting selectively with light in accordance with an image, design or character upon a resinous compound derived from B-naphthylamine and a five-membered mono-heterocyclic compound, and developing the print.

8. A photographic process which comprises: acting selectively with light in accordance with an image, design or character upon a resinous compound derived from furfural and B-naphthylamine.

9. A photographic process which comprises: acting selectively with light in accordance with an image, design or character upon a resinous compound derived from furfural and B-naphthylamine, and developing the print.

10. A photographic process which comprises: acting selectively with light in accordance with an image, design or character upon a compound which comprises a resinous material derived from an amine and a five-membered mono-heterocyclic compound, associated with a sensitizing agent.

11. A photographic process which comprises: acting selectively with light in accordance with an image, design or character upon a compound which comprises a resinous material derived from an amine and a five-membered mono-heterocyclic compound, associated with a sensitizing agent comprising a halogen source.

12. A photographic process which comprises: acting selectively with light in accordance with an image, design or character upon a compound which comprises a resinous material derived from an amine and a five-membered mono-heterocyclic compound, associated with a sensitizing agent comprising a halogen-liberating compound.

13. A photographic process which comprises: acting selectively with light in accordance with an image, design or character upon a compound which comprises a resinous material derived from an amine and a five-membered mono-heterocyclic compound, associated with a sensitizing agent comprising a halogen-substituted hydrocarbon.

14. A photographic process which comprises: acting selectively with light in accordance with an image, design or character upon a compound which comprises a resinous material derived from an amine and a five-membered mono-heterocyclic compound, associated with a sensitizing agent comprising iodoform.

15. A photographic process which comprises: acting selectively with light in accordance with an image, design or character upon a body which comprises a resinous compound derived from an amine and a five-membered mono-heterocyclic compound, said body having incorporated therewith a sensitizing agent, and developing the print.

16. A photographic process which comprises: acting selectively with light in accordance with an image, design or character upon a body which comprises a resinous compound derived from B-naphthylamine and a five-membered mono-heterocyclic compound, said body having associated therewith a sensitizing agent comprising a halogen-liberating compound.

17. A photographic process which comprises: acting selectively with light in accordance with an image, design or character upon a body comprising a resinous compound derived from furfural and B-naphthylamine, said compound having associated therewith a sensitizing agent comprising a halogen-liberating compound; and developing the print.

18. A photographic process which comprises: applying to a surface a film which comprises a solution of a resinous compound derived from an amine and a five-membered mono-heterocyclic compound; and acting selectively with light upon said film in accordance with an image, design or character.

19. A photographic process which comprises: applying to a suitable surface a film comprising a solution of a resinous compound derived from B-naphthylamine and a five-membered mono-heterocyclic compound; and acting selectively with light upon said film in accordance with an image, design or character.

20. A photographic process which comprises: applying to a suitable surface a film comprising a solution of a resinous compound derived from B-naphthylamine and a five-membered mono-heterocyclic compound, associated with a sensitizer acting selectively with light upon said film in accordance with an image, design or character; and developing the film.

21. A photographic process which comprises: applying to a suitable surface a film comprising a solution of a compound derived by combining an amine with a five-membered mono-heterocyclic compound, said solution containing also a sensitizing agent comprising a halogen-liberating compound; and acting selectively with light upon said film in accordance with an image, design or character.

22. A photographic process which comprises: combining B-naphthylamine with a five-membered mono-heterocyclic compound, incorporating in said compound a sensitizing agent comprising a halogen-liberating compound; acting selectively with light upon said compound in accordance with an image, design or character, to effect selective transformation of the compound; and developing the image.

23. The process of producing a photographic medium which comprises: incorporating with a resinous compound derived from an amine and a five-membered mono-heterocyclic compound, a sensitizing agent.

24. The process of producing a photographic medium which comprises: incorporating with a resinous compound derived from an amine and a five-membered mono-heterocyclic compound, a sensitizing agent comprising a halogen source.

25. The process of producing a photographic medium which comprises: incorporating with a resinous compound derived from an amine and a five-membered mono-

heterocyclic compound, a sensitizing agent comprising a halogen-liberating compound.

26. The process of producing a photographic medium which comprises: incorporating with a resinous compound derived from an amine and a five-membered mono-heterocyclic compound, a sensitizing agent comprising a halogen-substituted hydrocarbon.

27. The process of producing a photographic medium which comprises: incorporating with a resinous compound derived from an amine and a five-membered mono-heterocyclic compound, a sensitizing agent comprising iodoform.

28. The process of producing a photographic medium which comprises: forming a solution of a resinous product derived by combining an amine with a five-membered mono-heterocyclic compound, and incorporating in said solution a sensitizing agent.

29. The process of producing a photographic medium which comprises: forming a solution of a resinous product derived by combining an amine with a five-membered mono-heterocyclic compound, and incorporating in said solution a sensitizing agent comprising a halogen-liberating compound.

30. The process of producing a photographic medium which comprises: forming a solution of a resinous product derived by combining an amine with a five-membered mono-heterocyclic compound, and incorporating in said solution a sensitizing agent comprising a halogen-substituted hydrocarbon.

31. The process of producing a photographic medium which comprises: forming a solution of a resinous product derived by combining an amine with a five-membered mono-heterocyclic compound, and incorporating in said solution a sensitizing agent comprising iodoform.

32. A photographic medium comprising a resinous compound derived from an amine and a five-membered mono-heterocyclic compound, and a sensitizer associated with said resinous compound.

33. A photographic medium comprising a resinous compound derived from an amine and a five-membered mono-heterocyclic compound, and a sensitizer incorporated in said resinous compound comprising a halogen source.

34. A photographic medium comprising a resinous compound derived from an amine and a five-membered mono-heterocyclic compound, and a sensitizer incorporated in said resinous compound comprising a halogen-liberating compound.

35. A photographic medium comprising a resinous compound derived from an amine and a five-membered mono-heterocyclic compound, and a sensitizer incorporated in said resinous compound comprising a halogen-substituted hydrocarbon.

36. A photographic medium comprising a resinous compound derived from an amine and a five-membered mono-heterocyclic compound, and a sensitizer incorporated in said resinous compound comprising iodoform.

37. A photographic medium comprising a resinous compound derived from B-naphthylamine and a five-membered mono-heterocyclic compound, and a sensitizer incorporated in said compound.

38. A photographic medium comprising a resinous compound derived from B-naphthylamine and a five-membered mono-heterocyclic compound, and a sensitizer incorporated in said compound comprising a halogen source.

39. A photographic medium comprising a resinous compound derived from B-naphthylamine and a five-membered mono-heterocyclic compound, and a sensitizer incorporated in said compound comprising a halogen-liberating compound.

40. A photographic medium comprising a resinous compound derived from B-naphthylamine and a five-membered mono-heterocyclic compound, and a sensitizer incorporated in said compound comprising iodoform.

41. A photographic medium comprising a resinous compound derived from B-naphthylamine and furfural, said compound having incorporated therewith a sensitizing agent.

42. A photographic medium comprising a resinous compound derived from B-naphthylamine and furfural, said compound having incorporated therewith a sensitizing agent comprising a halogen source.

43. A photographic medium comprising a resinous compound derived from B-naphthylamine and furfural, said compound having incorporated therewith a sensitizing agent comprising a halogen-liberating compound.

44. A photographic medium comprising a resinous compound derived from B-naphthylamine and furfural, said compound having incorporated therewith a sensitizing agent comprising iodoform.

45. A photographic medium comprising a solution of a resinous compound derived from B-naphthylamine and furfural, said solution having incorporated therein a sensitizing agent.

46. A photographic medium comprising a solution of a resinous compound derived from B-naphthylamine and furfural, said solution having incorporated therein a sensitizing agent comprising a halogen source.

47. A photographic medium comprising a solution of a resinous compound derived from B-naphthylamine and furfural, said solution having incorporated therein a sen-

sitizing agent comprising a halogen-substituted hydro-carbon.

48. A photographic medium comprising a solution of a resinous compound derived from B-naphthylamine and furfural, said solution having incorporated therein a sensitizing agent comprising iodoform.

49. A photographic print comprising a resinous compound derived from an amine and a five-membered mono-heterocyclic compound and embodying an image, character or design.

50. A photographic print embodying an image, design or character which comprises a condensation product derived from an amine and a five-membered mono-heterocyclic compound.

51. A photographic print embodying an image, design or character comprising a condensation product of B-naphthylamine and furfural.

In testimony whereof we affix our signatures.

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