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PHOTOGRAPHIC MEDIA AND PROCESS.

No Drawing.

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This invention relates to photographic media and processes. The invention utilizes a wide range of hydrophobic colloids, in the nature of unsaturated compounds, which are capable of being transformed under the selective action of light transmitted, or projected, in accordance with a luminous image, design or character. In the invention, use is made of sensitizing agents and solvents. The sensitizing agents which are employed in association with the hydrophobic colloids, in accordance with the invention, preferably afford a source of halogen; and by preference, the sensitizer comprises a halogen-liberating compound which is adapted, under the action of light, to liberate halogen which apparently acts as a catalytic agent in effecting the selective transformation of the colloidal body by the selective action of light in accordance with an image, design or character. Also, the solvent medium employed should comprise a solvent, or mixture of solvents, which is capable of dissolving, or holding in suspension, both the hydrophobic colloid and the special sensitizer employed. Other characteristics which are desirable in such a solvent will be noted hereinafter.

According to the present invention, it is possible to utilize unsaturated organic compounds for photographic purposes. These unsaturated organic compounds, as indicated, afford hydrophobic colloids, which may be placed in solution and applied to suitable surfaces as coatings which are more or less sensitive to light, and are capable of being transformed under the selective action of light; and after such transformation, such coatings, or films, are capable of being developed, or fixed, in accordance with well-known methods, and in accordance with methods hereinafter pointed out. The selective action of light may occur by means of contact printing; or by optical projection, as will be readily understood by those skilled in the art. The result is a selective change in the state of the film by virtue of gelation, polymerization, or chemical change. These changes cause variations in the film proportional to the light action, and thus render the film suitable to be variably acted upon by suitable developers.

As intimated above, it is necessary, in connection with many of the hydrophobic col-

loids herein referred to, to employ suitable accelerating agents. On the other hand, some of the colloids are so light-sensitive that they may be employed for photographic purposes, without the use of a sensitizing agent. In any case, it is desirable to employ solvents which will give to the coating, or film, certain characteristics as hereinafter more particularly pointed out.

In addition to asphaltum and natural resins, referred to in a previously filed application, we utilize compounds which are derivatives of the carbocyclic, heterocyclic, or aliphatic series, of unsaturated compounds; and the invention comprises the use in photography of all and sundry equivalent compounds which may or may not be light-sensitive, and which may have their sensitivity increased by the addition of cooperating sensitizers.

In the present application, we claim photographic media and processes involving the use of a very wide range of hydrophobic colloids, combined with special solvents, with or without the use of special sensitizers.

In using the term unsaturated compounds we wish to define it in the broadest sense as used in organic chemistry to include not only olefine and acetylene linking in open chain compounds, but also in the rings of cyclic compounds, or between other atoms than carbon atoms in organic compounds such as carbon-oxygen and carbon-nitrogen linkages, etc., without limitations to unsaturated linkage between carbon atoms alone.

With these and other ends in view, we herewith describe such instances of adaptation as will disclose the broad underlying features without limiting ourselves to the specific details of procedure described herein.

Many substances show the effects of light so slightly that even under prolonged and intense luminous exposure they produce results which in and of themselves have no practical value in the photographic arts. These purely academic results might have remained scientific curiosities if we had not discovered the cooperating effect of suitable sensitizers which act catalytically or otherwise when incorporated with colloidal coatings. Such coatings are rendered many times more sensitive to light, thus reducing the time in which to secure practical photo-

graphic prints to seconds which heretofore required many minutes without attaining usable results.

The organic materials which we have found available as coatings in our process are of the most diverse chemical character. This is so marked that compounds chosen from any of the three general groups of unsaturated organic compounds, generally hydrophobic colloids of the carbocyclic series, heterocyclic series, or the aliphatic series, have been found useful with almost equally satisfactory results. Within these three general series we are not limited or restricted to a particular class of compounds; thus in the aliphatic group the following are instanced as being available for our purpose: hydrocarbons and materials composed in whole or in part of such compounds; unsaturated fatty acids, or their salts; esters of unsaturated alcohols or of unsaturated acids, including glycerides; condensation products, or polymerization products, formed by the interaction of aldehydes, ketones, or acid derivatives, with one another, or with phenols, or with ammonia, amines and related substances.

From the practical results that we have secured, it appears that, in a general way, we may select our materials from any class of organic compounds which are colloidal in nature, or are capable of being changed into a colloidal state by the action of light, providing that such materials are substantially hydrophobic, not easily soluble in water, which differentiates our process from such as used glue, gelatin, and the like substances. However, we do not exclude resin-like substances such as shellac, guaiacum, etc. In our use of the word hydrophobic, we mean any substances that are not readily soluble in water, but not necessarily the total absence of water.

As examples of some of the classes which provide available materials for our photographic process, the following are instanced as adaptations:

Carbocyclic series.

We have found that unsaturated carbocyclic compounds yield various light-sensitive substances. Certain synthetic resins may be formed by condensing phenols with aldehyde. Such condensation products, however, have little sensitivity to light, but when they are combined with suitable sensitizers, good prints have been secured in forty-five seconds and less. The reference to times of exposure as herein used are all based on the same source of illumination under identical optical conditions. The details of printing from negatives, etc., are such as are well known in the graphic arts. The source of illumination may be an arc light, high power nitrogen incandescent lamps or mer-

cury vapor tubes. In any case, for contact printing we may use solid or dry or wet coatings, and for printing by optical projection, we also use fluid, plastic or so-called wet coatings. Physical and chemical changes take place more rapidly in wet coatings than in dry, hence the former are usually the more sensitive.

Among accelerators used for these hydrophobic colloids are lead triethyl iodide, iodoform, mercury alkyls with iodine, and other metallic compounds.

Other resins, such as cumarone, are not appreciably sensitive to light, but this insensitiveness has also been removed by suitable sensitizers, such as iodoform, with which good prints have been obtained.

In the polyterpene group we have found a number of useful hydrophobic colloids as follows: (a) resins, kauri, etc., which in the case of kauri are sensitizable by means of iodoform; (b) a caoutchouc colloid may be sensitized by iodoform; and (c) gutta-percha can also be made sensitive to light through the use of lead resinate and iodine.

Carbocyclic hydrocarbons, such as naphthalene, through condensation yield useful derivatives. Thus, naphthalene and formaldehyde when condensed produce a hydrophobic colloid, which when sensitized with iodoform makes a material that is very sensitive to light. In fact, we have made successful exposure in fifteen seconds.

Other derivatives of the carbocyclic series are found in various dyes, such for instance as magenta. In some cases, these show a resinification accompanied by a change of solubility when exposed to light; this produces a transformation to a colloidal state and the final product is insoluble in water.

Heterocyclic series.

The heterocyclic class is typified by several groups such as the proteins, the alkaloids, synthetic resins such as those produced from furfural or pyrrol when condensed with acetone, naphthylamines, and other organic compounds.

The typical protein colloid, blood albumen, was sensitized by means of about 3% iodoform in an alcoholic solution. Under these conditions prints were obtained in about three minutes.

The alkaloidal substance, nicotine sulphate, diluted with benzol containing about 5% of iodoform, gave a material sensitive to light by projection under an exposure of five minutes.

The synthetic resins derived from monoheteratomic five-membered ring compounds—the furfural, pyrrol, thiophene group—by condensation, polymerization or otherwise, are in many cases very sensitive to light in and of themselves, so that additional sensitizing agents are not required.

Thus, a furfural-acetone resin without any sensitizer prints in thirty seconds. Another derivative is furfuramide which, when accelerated with iodoform, produces a print in three minutes. An alcoholic solution of furfuramide may be somewhat diluted by means of water, but the amide is dissolved with difficulty in water alone. Under the action of light the resinous film approaches the state of a hydrophobic colloid. The condensation product of B-naphthylamine with furfural, when sensitized by iodoform, produces rapid prints.

In this same class, analogous products may be derived from thiophene and pyrrol. These are merely illustrations of typical heterocyclic compounds found available, but which do not constitute limitations.

Aliphatic series.

Among the synthetic products of this series which may be used as colloidal polymers or alternatively when in the monomolecular state, are the vinyl compounds such as vinyl chloride, or which polymerize in light to a solid resinous film; this change is accelerated by iodine and it is possible to produce prints on such material in five minutes or less.

Asphaltum appears to be an unsaturated colloidal mixture insoluble in water, possibly derived from hydrocarbons of the aliphatic series. This material has been known as a light-sensitive medium since 1814, but has not come into general use on account of its very low sensitivity and the absence of means for greatly increasing the sensitivity and simplifying its development. Under the most favorable conditions, the minimum exposure time heretofore necessary for a line negative has been twenty minutes. By the use of special sensitizers, such as iodoform, we are able to produce prints from line negatives on an asphaltum coating in fifteen seconds.

Unsaturated aliphatic hydrocarbon derivatives may be prepared artificially by chlorinating and dechlorinating or otherwise treating the paraffines; this produces a dark viscous oil or tar that is also of a colloidal nature. In a practical sense it is non-actinic, but we have succeeded in making it responsive to light by adding iodine and lead resinate, thus enabling us to secure an image in about four to five minutes.

Among the unsaturated aliphatic acids and their derivatives, we have found acids, salts, and esters that are light-sensitive. Among the acids, oleomargaric acid becomes thickened when subjected to heat, and after being sensitized with iodine and a metallic salt forms a coating on which prints can be secured in two minutes. Among the salts we have succeeded in sensitizing lead oleate or lead tungate with iodine so as to produce

prints in one minute. The esters or glycerides, such as perilla oil, tung oil, menhaden oil, etc., are responsive to varying degrees of luminosity and by proper treatment and the addition of cooperating accelerators will, when exposed to a luminous image, produce various degrees of solubility in the coating, representative of the image, in a fraction of a second. The foregoing comprehensive list of hydrophobic organic colloids is sufficient to illustrate the wide variety of such substances available for the purpose of the invention.

Sensitizers.

In our use of the designation "sensitizers" we include materials of a diverse nature, all of which increase the responsiveness to light of hydrophobic organic colloidal coatings. Among various available materials, we have found that the very important ones are the halogens, among which iodine is most adaptable. In some cases it can be used in a free state and in other cases compounds of iodine must be used which will freely liberate iodine when they are exposed to light. Examples of these are tetraiodopyrrol, lead triethyl iodide, mercurous iodide, etc. Iodoform is decomposed under the influence of light in the presence of available oxygen, so as to give up iodine, carbon monoxide, carbon dioxide, and water. Iodine, when exposed to light, is singularly activated; in which state it is able to accelerate condensations, polymerization, halogenation, substitutions, etc., causing selective changes in the structure of the coating under the action of light which may be permanently fixed by a suitable development of the impressed image. Bromine is also a powerful sensitizer, and in some cases when bromine and iodine are combined and a coating sensitized therewith, the sensitizing effect is about five times that of the iodine alone.

There are other materials which greatly increase the efficiency of the haloid sensitizers. These may be considered as auxiliary accelerators. Chief among them are compounds of several metals and the organic salts are most conveniently employed. These may comprise resinates, oleates, etc. The useful metals are those whose halides are insoluble in the medium and which are poly-valent, e. g., lead, mercury, nickel, copper, cobalt, etc. Phosphorous has an accelerating effect and fluorescent dyes, such as rhodamine 6G, phenosafrano, etc., also increase the sensitivity. In other cases, notably with the unsaturated glycerides, traces of picric acid cooperate most effectively with the halides to increase their sensitivity.

Minor accelerators, such as solid oxides, halides, carbonates, etc., may be used. Such

substances among others include ferric oxide, zinc oxide, lead peroxide, lead iodide, mercurous iodide, barium carbonate, etc.

An important cooperating effect is also produced by the supporting surface. This may be due to catalysis or dependent on the degree of reflection of the surface on which the coating is placed. For instance, most coatings print more rapidly on silver, aluminum, or zinc plates than on copper, brass, gold, etc., but these cooperative effects are not specifically claimed herein.

Development.

In the use of our process the technique of development is probably purely physical. The developers are chosen for different substances used as coatings so as to take advantage of the changes produced in the coatings through the action of light. These changes are all of a selective order. They appear to be due to variations in viscosity, solubility, porosity, absorptiveness, etc. The image may be made visible through the removal of those parts of the coating that have not been acted upon by the light, or vice versa, through the removal of these parts which have been acted upon by the light, or through the selective absorption of suitable stains, dyes, etc., without the removal of any of the coating.

The variations described above produced selectively by a luminous image in our coating may be taken advantage of by development in several ways. When the coating changes from a sol, oily, viscous or "tacky" condition to a gel, plastic or hard solid state, then the image may be developed in the case of an oleaginous coating by simply washing it with soap and water; or, alternatively, by placing a transferring surface in contact with the exposed plate; on its removal, there is found on it the soft imprinted areas of the coating which adhere thereon. Under solubility changes, we include "reversibility" which implies that our colloidal coating has become inversely selective to a specific solvent. Development on this basis consists, in its simplest form, in immersing the exposed plate in suitable baths, e. g., a print with a fural-acetone coating is developed by bathing it in a mixture of turpentine and benzol, and subsequently rinsing it with water. With certain coatings, such as bitumen, it is found desirable to use more or less abrasion. This is usually done by gently rubbing on oleic acid solution over the exposed surface. It is also possible to lay absorbent paper over a print and apply a solvent to the back of such paper when the soluble portions of the image will be taken up selectively by the capillarity of the paper and the remaining portions of the print may be treated in any desired manner.

In some cases printed films composed of certain colloidal coatings are not easily developed by solvation; but these show a marked degree of absorption for dyes, taking up color from a cooperating dye with which the exposed image is washed. This absorption is selectively proportional to the action of the light to which the coating has been exposed. Among such dyes, we have found a solvent naphtha oil red stain to be available for this kind of development.

Our coatings, after exposure to luminous images, are usually found to be selectively permeable or to have a selective porosity, so that a metallic plate to which the coating is applied can be etched in variable relief approximately proportional to the variation in light and shade of the image. By reason of this fact, an acid reagent will more quickly reach the metallic surface beneath the coating where such coating is quite porous. Because of this difference in time when certain parts of the plate are first attacked by the acid, the etching will produce a variable relief surface without the dots, lines, etc., if a continuous unbroken change in relief is desired. On the other hand, if such an etching is desired for photo or rotogravure purposes, then intersecting lines, on the completed plate may be used. These serve to assist in holding ink against removal when the surplus is wiped off before printing.

This porosity is true of most unsaturated colloidal coatings. In some cases a certain solvent, in a selective manner, will only develop the image by the physical removal of the coating; while another solvent frequently produces development only through selective porosity by a differential effect on the surface to which the coating is applied, or by a variable change in the coating itself.

As instances of adaptation found to successfully operate with the unsaturated group of hydrophobic organic colloids, we present the following as exemplifications only and not as limitations. These relate to derivatives which are mentioned in the same order as that to which they have been hereinbefore referred.

In addition to the previously mentioned exemplifications, we have also found the following to give good results. These are not, in any sense, limitations, but are, instead, instances of the adaptability of our process. They relate to the carbocyclic, heterocyclic and aliphatic series of compounds.

In the carbocyclic series, we have used 12 grams of phenol, 30 grams formalin and 2.7 grams of sodium acetate which were mixed together and heated to about 150 degrees C., for approximately four and one-half hours. The resulting product is decanted and dried. A solution of this resin-like substance was sensitized with 2% iodine in benzol, or with

lead triethyl iodide, or alternatively with iodoform. Coatings of this material produced prints in three minutes or less which were developed in alcohol and water.

5 In another exemplification we have used 30 grams of formalin and 20 grams of B-naphthylamine to form an addition product at room temperature. 20 grams of the dried precipitate was dissolved in acetone to make
10 a 20% solution. When this was sensitized with 10 grams of iodoform, we produced prints in fifteen seconds.

An additional exemplification, using naphthalene and formaldehyde, was carried
15 out as follows: 100 grams of naphthalene was mixed with 80 grams of formalin and 120 grams of concentrated sulphuric acid. This was heated for three hours in a reflux condenser and the resulting resin was
20 washed with water and a caustic soda solution. A 20% solution in benzol was sensitized with 5% iodoform which resulted in a sensitivity that permitted us to produce prints in two minutes which were developed
25 in 50—50 turpentine and benzol.

In the use of a natural kauri resin sensitized with iodoform, the acetone or benzol insoluble portion of kauri is dissolved in ethyl methyl ketone and, when sensitized
30 with 5% of iodoform, permits of prints being produced in five minutes.

In the heterocyclic series, we instance the following exemplifications: 90 grams of furfural mixed with 58 grams of acetone and
35 100 grams of a 50% solution of caustic soda in water is heated in a reflux condenser for thirty minutes producing a resinous product that is itself sensitive to light to such an extent that prints are produced in thirty
40 seconds.

In an additional exemplification, we have used 100 grams of furfural mixed with 100 grams of concentrated ammonium hydroxide at room temperature or with slight heating.
45 This produced a resin which, when dried and dissolved in benzol, was of itself sensitive enough to give prints in five minutes, but when sensitized by means of iodine, iodoform, ammonium dichromate, etc., produced prints in about half the previous
50 time.

In the aliphatic series, we have found that vinyl benzene, when subjected to steam distillation with storax, produced a distillate, which, when combined with benzol
55 to form about a 15% solution, was sufficiently self sensitive to produce a print by projection in ten minutes; but when sensitized with iodine, prints were procured in three
60 minutes.

In another exemplification, we have used asphaltum 10%, solvent naphtha 40%, benzine 25% and sensitizer 25%. The sensitizer is made by mixing ethyl methyl ketone 22%,
65 iodoform 12%, solvent naphtha 65½% and

concentrated ammonium hydroxide ½%. With this procedure, we have successfully produced good prints in fifteen seconds.

We have found, also, that the following exemplification of another aliphatic derivative of the esters produces practical results,
70 on coated brass, in forty seconds; and in twenty seconds on aluminum. In this exemplification the following ingredients were used; tung oil 22.7%, lead resinate 1.35%,
75 lead triethyl iodide 9.1%, iodoform 1.35%, benzol 44% and solvent naphtha 25%. The iodoform sensitizer, which is added after the addition of the colloid base, produces a mixture devoid of free iodine. It is very sensi-
80 tive to light, under the influence of which, it decomposes rapidly, precipitating lead iodide.

The coating to which the above sensitizer is added constitutes a varnish-like substance
85 of tung oil, lead resinate, and a solvent. This oil varnish is added to the solution of the lead triethyl iodide in benzol, and the iodoform is dissolved in this mixture. The advantage of the above sensitizer consists
90 in the absence of free iodine, which, by preventing the areas that are unacted upon by the light from becoming insoluble, results in prints of great clearness and maximum contrast, without sacrificing the re-
95 quired tonal gradations.

As an example of the relation of exposure to areas, we have found that an increase of 4.8 in area requires an addition of 1.33 in exposure, starting with an area of 1 and
100 an exposure of 1. An increase of area to 10.2 only increases the exposure to 2, and a further increase of area to 150 only raises the exposure to 9, which is of great practical value in making enlargements of any
105 kind for lithographic posters, etc.

We are unable to state, and the literature on the subject is silent regarding, the theoretical explanation of many of the reactions which take place in the practice of
110 our process. Whatever divergence there may be between any theoretical hypothesis that we have advanced and any ultimate determination of authenticated technique, reactions, etc., relating to the same, we do not limit
115 ourselves to any hypothesis that has been used, for the reason that the practical disclosures we have made lay the necessary ground for protection in the realm of organic compounds instanced herein.
120

In previously filed applications, to which we are parties, there have been described, more in detail, numerous examples which are set forth in the present application, and additional examples, also, have been
125 given in the previous applications. This applies to the use of various hydrophobic colloids which are capable of being transformed under the selective action of light, with subsequent development of the film.
130

Also, in previous applications, there have been given illustrations of the use of special solvents in many special cases.

In the present application, we have heretofore made mention of the use of various solvents, including alcohol, benzol (benzene), acetone, ketones, benzine, solvent naphtha, and mixtures of such solvents. Among the solvents mentioned, benzol and solvent naphtha are examples of aromatic hydrocarbon solvents, derived chiefly from coal tar products. Such solvents are useful, especially, in the media and processes herein described. For example, benzol, solvent naphtha, or a mixture of these materials, affords a solvent medium which is a common solvent for the hydrophobic colloids and for the accelerating agents, which the invention employs. Thus, by way of specific example, benzol is a solvent for these hydrophobic colloids and also is a solvent for iodoform, iodine, etc.; and, as has been indicated, the halogen-supplying sensitizers are the ones which have been found most useful.

It is desirable that the solvent employed shall not only be capable of dissolving and holding in solution the hydrophobic colloids and the sensitizer, when employed, but the solvent should also be such as to produce a solution which can be freely flowed, or whirled, upon a suitable surface, which will not result in streaks, which will largely evaporate within a short period, and which will yield a tenacious and resistant uniform film capable of being readily printed and developed. Also, it is desirable that the solvent shall be inexpensive and readily procurable on the market. The aromatic hydrocarbon solvents, and especially, benzol, fulfill, in a remarkable degree, the requirements. It may be added that while less desirable solvents may be employed in some cases, it is advisable, where possible, to employ a solvent in which the sensitizing agent will not decompose. For example, while alcohol may be used in some cases to place iodoform in solution, there is danger that iodoform will decompose when in alcoholic solution, even in the dark. This is true to some extent of the ketones, including acetone and ethyl methyl ketone. For reasons of this kind, it is desirable to employ solvents of the aromatic hydrocarbon class, such as benzol, solvent naphtha, or a mixture of these materials.

It may be added that when the most suitable solvent is employed, a small quantity of the solvent is strongly adsorbed by, and remains in the coating indefinitely, and the quantity and character of this remaining solvent influences, markedly, the character of the coating, its speed of printing, and its capability of being developed. Benzol, for example, possesses this property to a very

strong degree, while alcohol, for example, possesses such property in a very minor degree. That is, the tendency of alcohol, or similar solvents, is to evaporate almost completely from the coating, and leave a more or less friable coating, which is less desirable than the tenacious coating which results when benzol, for example, is used. These remarks apply more particularly to the hydrophobic colloids which we have thus far found to be most desirable for use in the improved media and processes, but it is to be borne in mind that other solvents, such as the ketone, alcohol, or other solvents, may serve useful purposes in special instances.

The foregoing 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. The process of preparing a photographic medium which comprises: combining with a synthetic resin hydrophobic colloid capable of transformation by the selective action of light a solvent medium comprising an aromatic hydrocarbon solvent.

2. The process of preparing a photographic medium which comprises: combining with an artificial hydrophobic colloid capable of transformation by the selective action of light, a solvent medium comprising benzol and solvent naphtha.

3. The process of preparing a photographic medium which comprises: combining with a hydrophobic colloid capable of transformation under the selective action of light an organo halogen-liberating sensitizer and a solvent medium comprising an aromatic hydrocarbon solvent.

4. The process of preparing a photographic medium which comprises: combining with a hydrophobic colloid capable of transformation under the selective action of light an organo halogen-liberating sensitizer and a solvent medium comprising benzol.

5. The process of preparing a photographic medium which comprises: combining with a hydrophobic colloid capable of transformation under the selective action of light an organo halogen-liberating sensitizer and a solvent medium comprising benzol and solvent naphtha.

6. The process of preparing a photographic medium which comprises: combining with a hydrophobic colloid capable of transformation under the selective action of light a sensitizer comprising a halogen-substituted hydrocarbon and a solvent medium comprising an aromatic hydrocarbon solvent.

7. The process of preparing a photographic medium which comprises: combining with a hydrophobic colloid capable of transfor-

mation under the selective action of light a sensitizer comprising iodoform and a solvent medium comprising an aromatic hydrocarbon solvent.

5 8. The process of preparing a photographic medium which comprises: combining with a hydrophobic colloid capable of transformation under the selective action of light a sensitizer comprising iodoform and
10 a solvent medium comprising benzol.

9. The process of preparing a photographic medium which comprises: combining with a hydrophobic colloid capable of transformation under the selective action of
15 light a sensitizer comprising iodoform and a solvent medium comprising benzol and solvent naphtha.

10. A photographic process which comprises: acting selectively with light, in accordance with a luminous image, design or character, upon a coating comprising a synthetic resin hydrophobic colloid capable of transformation under the action of light, associated with a solvent medium comprising
20 an aromatic hydrocarbon.

11. A photographic process which comprises: acting selectively with light, in accordance with a luminous image, design or character, upon a coating comprising a synthetic resin hydrophobic colloid capable of transformation under the action of light, associated with a solvent medium comprising
25 benzol and solvent naphtha.

12. A photographic process which comprises: acting selectively with light, in accordance with an image, design or character, upon a coating comprising a hydrophobic colloid capable of transformation under the action of light, an associated halogen-liberating sensitizer, and a solvent medium comprising an aromatic hydrocarbon solvent.
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13. A photographic process which comprises: acting selectively with light, in accordance with an image, design or character, upon a coating comprising a hydrophobic colloid capable of transformation under the action of light, an associated halogen-liberating sensitizer, and a solvent medium comprising benzol.
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14. A photographic process which comprises: acting selectively with light, in accordance with an image, design or character, upon a coating comprising a hydrophobic colloid capable of transformation under the action of light, an associated halogen-liberating sensitizer, and a solvent medium comprising benzol and solvent naphtha.
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15. A photographic process which comprises: acting selectively with light, in accordance with an image, design or character, upon a coating comprising a hydrophobic colloid capable of transformation under the action of light, a sensitizing agent comprising iodoform, and a solvent medium comprising an aromatic hydrocarbon solvent.
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16. A photographic medium comprising a solution of a synthetic resin hydrophobic colloid capable of transformation under the action of light and a solvent medium comprising benzol.

17. A photographic medium comprising a solution of a hydrophobic colloid capable of transformation under the action of light and a solvent medium comprising benzol and solvent naphtha.

18. A photographic medium comprising a hydrophobic colloid capable of transformation under the selective action of light, a sensitizing agent comprising a halogen, and a solvent medium comprising an aromatic hydrocarbon solvent.

19. A photographic medium comprising a hydrophobic colloid capable of transformation under the action of light, a sensitizer comprising a halogen-liberating compound, and a medium comprising an aromatic hydrocarbon solvent.

20. A photographic medium comprising a hydrophobic colloid capable of transformation under the action of light, a sensitizer comprising a halogen-liberating compound, and a solvent comprising benzol.

21. A photographic medium comprising a hydrophobic colloid capable of transformation under the action of light, a sensitizer comprising a halogen-liberating compound, and a solvent comprising benzol and solvent naphtha.

22. A photographic medium comprising a hydrophobic colloid capable of transformation under the action of light, an organo halogen-liberating sensitizer, and a solvent medium comprising an aromatic hydrocarbon solvent.

23. A photographic medium comprising a hydrophobic colloid capable of transformation under the action of light, a sensitizer comprising iodoform, and a solvent medium comprising an aromatic hydrocarbon solvent.

24. A photographic medium comprising a hydrophobic colloid capable of transformation under the action of light, a sensitizer comprising iodoform, and a solvent comprising benzol.

25. A photographic medium comprising a hydrophobic colloid capable of transformation under the action of light, a sensitizer comprising iodoform, and a solvent comprising benzol and solvent naphtha.

26. A photographic print comprising a hydrophobic colloid associated with a sensitizing agent comprising a halogen, and a solvent medium comprising an aromatic hydrocarbon solvent, said hydrophobic colloid embodying an image, design or character.

In testimony whereof we affix our signatures.

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