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MATERIAL FOR USE IN A PHOTOGRAPHIC REPRODUCTION SYSTEM

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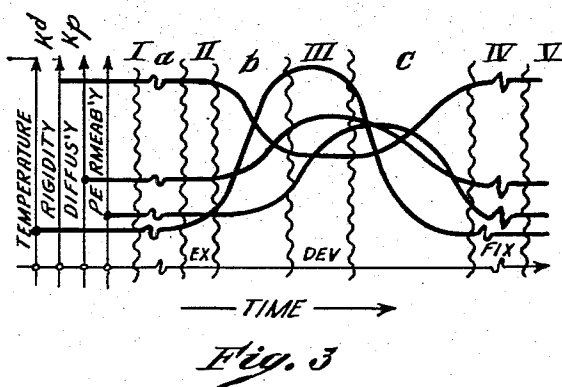
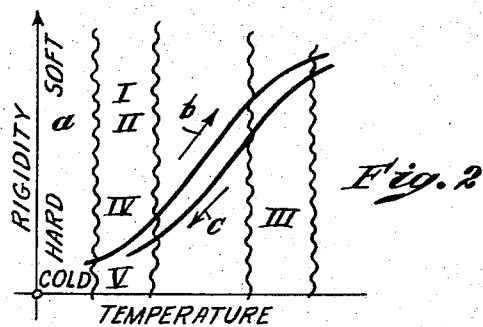
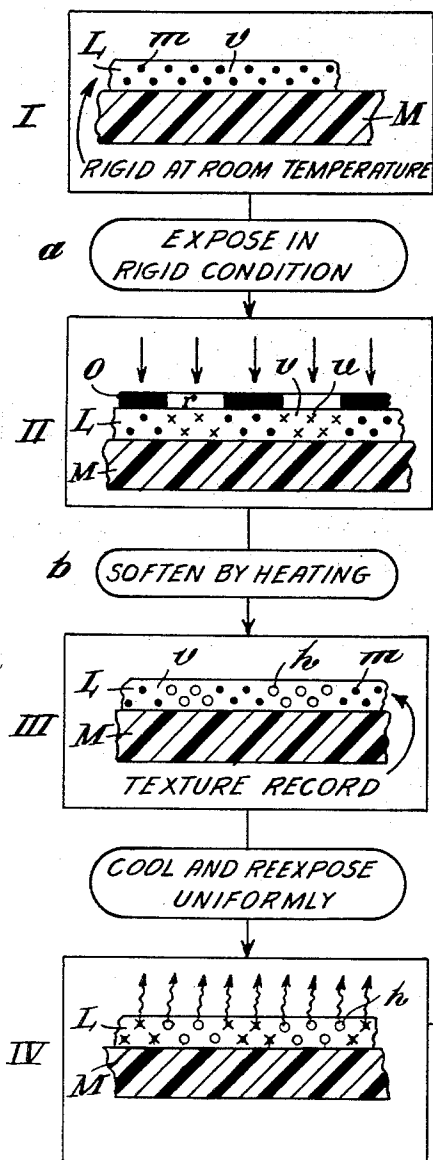


Fig. 1

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MATERIAL FOR USE IN A PHOTOGRAPHIC
REPRODUCTION SYSTEM

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3 Claims. (Cl. 96—75)

This invention relates to the copying of records such as printed matter or photographic originals including microfilm, by means of compounds which produce gas upon irradiation, and particularly to printing material for forming such copies and to the copies themselves.

Primary objects of the present invention are to provide laminated photographic reproduction blanks of the above type in which a base or support and a photosensitive coating adhere more firmly to each other than those of previously known blanks, to provide such a blank in which a record can be more rapidly and easily rendered permanent, to provide such blank material which permits of more accurate temperature control during exposure and which is more stable than materials heretofore known, and to provide essentially permanent photographic prints in terms of purely physical textural modification of the coating.

A further object of the invention is to provide photographic reproductions according to a technique which is inexpensive, extremely simple, particularly reliable as to stability, and which permits satisfactory operation with a minimum of effort of unskilled labor and in minimum time.

Additional objects are to provide a reproduction technique suitable for offices and the like which is dry throughout and does not require chemical treatment or rinsing baths, and which optionally permits the direct printing of either negative or positive copies with the same material, apparatus and general procedure.

In summary, the substance of the main aspects of the invention is as follows. A material for forming a photographic record in terms of substantially purely textural change comprises a durable support having a coating thereon of a thermoplastic colloid constituting a vehicle containing dispersed therein a sensitizer substance such as light sensitive diazo compounds, which generates sources of gas upon exposure to radiation, which sources are capable of causing the said textural change, the support material adhering strongly to the vehicle, being transmissive to infrared radiation, and stable over a wide temperature range. A preferred support material which is especially valuable in the above combination is the reaction product of ethylene glycol and terephthalic acid which produces a polyester film marketed by E. I. du Pont de Nemours & Co., Wilmington, Delaware, under the trade name "Mylar." This material is used as a support for the above characterized photolytic colloid material is particularly satisfactory in providing a combination which, according to the invention, has strong adherence between support and vehicle, and which is transparent to a wide spectrum and stable over a wide temperature range.

These and other objects and aspects of novelty will appear, in addition to those contained in the above summary of the invention indicating its nature and substance including some of its objects, from the herein presented outline of its principles, its mode of operation and its practical possibilities, together with the following de-

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scription of a typical embodiment illustrating its characteristics. These refer to drawings in which

Fig. 1 is a flow diagram of a printing process employing and resulting in material according to the present invention;

Fig. 2 is a temperature-plasticity characteristic of the vehicle according to the invention; and

Fig. 3 is a diagram of the changes of temperature, plasticity, diffusivity, and permeability of the vehicle within the time cycle of a process according to Fig. 1.

The properties of the printing material according to the invention depend mainly upon its use, and it can best be described in terms of such use. Therefore, a typical example of a printing technique especially suited for the new material will first be shortly described with reference to the flow diagram of Fig. 1. The physical events involving the vehicle during such a process are illustrated in Figs. 2 and 3, and the process steps of the flow diagram and the corresponding portions of Figs. 2 and 3 are similarly labeled.

In block I of Fig. 1, a layer of vehicle material is indicated at L with the support material M. This material L comprises a thermoplastic vehicle v with molecules or molecule groups m of photolytic substance (hereinafter shortly referred to as sensitizer) incorporated therein. In storage and during handling (with the sole exception of the developing stage) it is comparatively hard, corresponding to low, such as average room temperature. As indicated at a and in block II, the material L in that indurated condition is exposed to an original O, such as a microfilm or other transparency. The printed or other record matter of original O is indicated by dark portions r . The exposure can be accomplished by contact printing as indicated at II, or by means of a conventional projection printer. It is possible to make copies of the same as well as of opposite photographic signs, in the sense that printing with the same sign means making a positive from a positive or a negative from a negative, whereas negative and positive are of opposite sign.

Preferred sensitizers are essentially sensitive to radiation within the 300 to 500 millimicron range which permits handling in ordinary room light or at least in incandescent light.

The exposed sensitizer generates gas molecules which do not necessarily constitute a gas for purposes of the process. However due to the properties of the vehicle the gas diffuses internally to form gas units u which for present purposes can be considered to constitute the smallest possible bodies which will perform in the manner of a true gas. The exact reason why units form at a given point is not altogether clear but the unit loci are unquestionably codetermined by lattice singularities which can be controlled to a certain extent by selection of the vehicle material and also built into the latter. The original O is thus copied with opposite sign in terms of invisible units u constituting a latent record.

The vehicle v of the layer L is then softened by raising its temperature, which induces record development by disrupting the original lattice or general internal texture of the vehicle due to expansion of the gas units u . This expansion is indicated by gas vesicles, bubbles or holes h , although it is understood that the textural change which results in a light refracting and reflecting pattern within the vehicle is not necessarily due to bubbles in the conventional sense of that term. At III, the layer L now contains a developed record, corresponding to that of the original O, in terms of visible bubbles or cavities containing gas. Sensitizer molecules m remain in the unexposed portions.

The heating of layer L can be accomplished by any convenient means, for example placing on a hot plate

which is by a thermostat maintained at the temperature especially suitable for the vehicle material in question.

In order to fix the record, a uniform exposure can be applied as indicated at *c*. This exposure activates the remanent photolytic sensitizer, that is the sensitizer in the initially unexposed portions. The gas units escape through the layer L as indicated at IV. Upon completion of the permeation a permanent record is obtained as illustrated at V.

For purposes of invention, the properties of vehicle, sensitizer and support materials are essential with a view to optimum cooperation, and therefore the vehicle sensitizer and support desiderata will now be shortly discussed.

The vehicle can be selected primarily with a view to absolute independence from moisture whether due to climate or accidental application in which case certain synthetic thermoplastic colloids are selected, or the criterion can be low price and ease of handling in which case natural organic colloids such as gelatin are chosen.

The operating temperatures of these vehicles should be such that the material is easy to handle and independent of climate. Two working temperatures only are required; one within a fairly wide range of room temperatures, and the other well above any ambient temperature likely to be encountered. This higher temperature is needed only during a short time for development, but the support must be stable up to that temperature. In certain instances, vehicles are permanently hardened at temperatures above the development temperature, and the support must then withstand these higher temperatures.

It was found that proper formation of the latent as well as permanently visible records depends primarily upon three distinct properties of the vehicle, namely the diffusivity for gas formed therewithin, the permeability for gas to escape to the atmosphere, and the rigidity against shape distorting flow.

The diffusion of gas within the vehicle makes possible the record formation and determines the photographic character (such as definition, density and contrast) of the record, formed therein in terms of gas sources, units and cavities. The permeation of gas is its transfer by diffusion through the vehicle from a singular point of higher pressure such as herein referred to as a cavity, hole or bubble, to one of lower pressure, such as the atmosphere. The permeation characteristics are instrumental mainly with regard to the fixation of the record, in determining the speed and completeness of removal of gas from the vehicle in order to prevent uncontrolled record formation subsequent to the intended exposure. The rigidity (or its reciprocal the plasticity) as a phenomenon dependent upon the degree of molecular flow of the vehicle itself as a function of temperature, is directly instrumental in determining the bubble expansion and size, and indirectly as one of the factors that control diffusion and permeation of the gas; it also determines the macroscopic mechanical properties of the record sheet.

Diffusivity can be mathematically defined as a function of temperature and material constants; permeability is a function of diffusivity and pressure gradient. Since formulas of this type depend largely on critical constants it is best to evaluate these phenomena experimentally and to express them in arbitrary units, for purposes of the diagram referred to below for example *Kd* for diffusivity and *Kp* for permeability, the dimensions of which are of the nature of a velocity and of a flow, respectively.

The rate of diffusion of the gas within the vehicle varies between an upper and lower limit. The lower limit of diffusion is determined by the need for gas to move with sufficient freedom to obey Boyle's and Charles' law relating the volume to pressure and temperature respectively, after the release, from the sensi-

tizer, of the gas sources *s*. These sources can be conceived as single gas molecules or groups thereof, but at any rate they do not yet form units of a true gas such as shown at *u* of Fig. 1.

The rigidity characteristics of the vehicle, apart from general utility considerations, must conform to the above requirements regarding diffusion and permeation during the principal steps of the present technique, namely exposure, development and fixation.

These requirements are schematically indicated in Fig. 2 as follows. The low temperature range marked I, II, IV and V represents a rigid yet permeable phase which is the normal condition, also employed during exposure. In range III the vehicle is relaxed permitting the gas expansion during development, which is interrupted by cooling when the desired record in terms of vehicle disruption is obtained. Fig. 2 indicates the reversibility of this cycle. It will be noted that the labels applied to Fig. 2 relate this diagram to Fig. 1, regions I and II prevailing during exposure, region III during development, and regions IV and V during fixation and afterwards.

The determination and control of the vehicle and support properties is accomplished (apart from the operational temperature adjustment during the printing process as above-described) by proper selection and composition of the vehicle and the support in relation to the nature of the gas generated by the photolytic sensitizer employed, and the process desiderata.

Thermoplastic vehicle material which is suitable for the above purpose can be selected from a variety of classes, regardless of chemical origin, the requisite properties being purely of a physical nature. The vehicle can be a natural organic colloid such as gelatin or a water inert, i.e. hydrophobic, synthetic colloid suitable for incorporation of a desirable sensitizer either mechanically such as by way of a ball mill or by means of appropriate solvents. Examples will be presented below.

The sensitizer materials most suitable for use in the present invention are of the so-called diazo type which upon oxidation liberate nitrogen gas. Among such sensitizing substances are p-NN-dimethylaminobenzene-diazonium zinc chloride and 1-dimethylamino-4-naphthalenediazonium fluoborate which were found to be particularly valuable, but the following substances were also found to be practical:

p-Anilinobenzenediazonium sulfate
p-NN-diethylaminobenzenediazonium zinc chloride
p(N-ethyl-N-hydroxyethylamino) benzenediazonium zinc chloride
p(N-ethyl-N-methylamino) benzene diazonium zinc chloride
4-diazo-3-oxynaphthalene sulfonic acid
4-NN-diethylamino-5-methylbenzenediazonium chloride

The support material according to the invention is characterized by properties making it especially suitable in combinations with vehicles and sensitizers of the above nature, as follows.

The adherence between vehicle and support materials is stronger than that between conventional materials, especially when the colloid vehicle is a water inert thermoplastic resin such as will be more fully described below.

One practical mode of fixing a developed record is its exposure to ordinary actinic light. This sufficiently actuates any remanent sensitizer in the record area as well as the sensitizer in the heretofore unexposed areas to form gas units which then permeate through the colloid, thus permitting complete fixation.

The optical transmission characteristics of the support are of primary importance. Lack of absorption in the infrared range is particularly beneficial since a base which absorbs and accumulates radiant heat tends to

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start development prematurely and otherwise interferes with the positive and exact temperature control which is essential in fixing techniques of the present type. Good transmission through the visible to the ultraviolet range is important, especially if it is desired to use this material as an original for making further copies by the same or other processes. High optical clarity is desirable for purposes of ultimate use in projectors or viewers, and of making third and fourth generation copies with the present technique.

A further requirement is heat stability within a range from subzero storage temperatures to approximately 300° F. which upper limit not only accommodates the development or hardening temperatures of all otherwise suitable vehicle materials, but permits the shortening of the development period by way of a steeper temperature gradient, in addition to its shortening due to the permeable support. Conventional bases such as cellulose acetate become mutable at such temperatures.

It was discovered within the purview of this invention that the synthetic material "Mylar," identified hereinabove, fulfills the above physical requirements to a surprisingly complete extent and is therefore especially suited for purposes of a technique of the present type which depends on the permeation of a gas, on temperature control and on the limited sensitivity to radiation a photolytic agent. The following table illustrates these superior qualities of "Mylar" as compared to conventional bases.

Printing Stock.....	Gelatin on Cellulose Acetate	Gelatin on Mylar	Synthetic (Saran) on Mylar
Stock Characteristic			
Strength of Bond.....	fair.....	good.....	good.
Physical Condition at Degrees F.:			
100.....	good.....	good.....	excellent.
200.....	fair.....	good.....	good.
300.....	poor.....	good.....	(?),
Light Transmission Properties.....	good.....	excellent..	excellent.

¹ Saran is not used at this temperature.

It will be understood that records of the present type, in terms of textural change of a photolytically sensitive layer will appear dark in transmitted light and bright on an opaque ground; hence, the advantageous transmission properties of supports of the "Mylar" type are particularly useful in the case of transparencies.

Two specific embodiments of the invention are as follows.

Example I.—Gelatin vehicle on "Mylar" support

100 grams of high-grade dry gelatin such as is sold under the trade designation "Kodak Peabody Gelatin" is soaked for two hours in 1900 ml. distilled water of 30° C. To this is added 8 grams citric acid C.P. and 10 grams of the sensitizing substance sold under the trade designation "Edwal Compound #8" which is a zinc salt of paradiazo dimethylaniline. This is diluted to make 2000 ml. and the emulsion coated on a "Mylar" support by conventional means to a thickness of about 0.8 mil to 1 mil rather less than more, depending on process control details and record requirements not material to the present invention.

The "Mylar" supported blank is exposed to an original in direct contact therewith. For contact printing on microfilm strips, a General Electric Co. 100 watt lamp, type AH4 is used in a continuous printer running at 10 feet per minute. Development is carried out in the same machine by subsequent passage of the film through a heating element at about 250° F. It will be understood that the exact processing data depend a good deal upon the original to be copied and on various secondary factors, so that the usual trial runs will have to be made when new conditions are encountered.

A preferred fixing procedure adopted to prevent sec-

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ondary development upon exposure to fairly intense radiation such as sunlight or the lamp of a viewer, is practiced as follows. Subsequent to development and cooling of the vehicle, it is by itself run again through the exposure drum of the above-mentioned printer but not through the heater. The material is then stored in a cool place for about one hour which allows the gas to permeate to the atmosphere, completing the fixing.

Example II.—Synthetic vehicle on "Mylar" support

Certain synthetic thermoplastic vehicle materials coming within the scope of the present invention are immediately available for use in conjunction with a "Mylar" support and these include polystyrene, polyvinyl chloride, copolymers of vinyl chloride and vinyl acetate.

Materials available directly for purposes of vehicle are, however, not very abundant and often undesirable for extraneous reasons such as physical properties apart from those required for purposes of the present invention. Accordingly, vehicle materials which are not directly suitable for optimum results are rendered so suitable by use of auxiliary admixtures referred to as modifiers of which the following formula is illustrative.

Function	Component	Parts by Weight
Vehicle.....	Saran F-120 (200 Cps.).....	16.0
Modifier.....	Acryloid A101.....	4.0
Sensitizer.....	Edwal Compound #8.....	1.2
Solvent.....	Methyl Ethyl Ketone.....	60.0
Solvent.....	Methyl Alcohol.....	12.0

Saran F120 is a vinyl type resin made by and available from the Dow Chemical Company, and described as a copolymer of vinylidene chloride and acrylonitrile.

Acryloid A-101 is a polymethyl methacrylate made by and available from Rohm and Haas as a 40% solution in methyl ethyl ketone. The weight given above is calculated on the amount of resin only.

Edwal Compound #8 is p-NN-dimethylaminobenzene-diazonium zinc chloride supplied by the Edwal Laboratories Inc. of Ringwood, Illinois.

The methyl alcohol is warmed, to approximately 50° C. and the Edwal Compound stirred in. This solution is then diluted with 5 cc. of methyl ethyl ketone and slowly added while stirring, to a solution of the two resins Saran and Acryloid in the remainder of methyl ethyl ketone, this latter solution being likewise warmed to 50° C.

The above composition is cast on a "Mylar" base to a dry coating thickness of about ½ to ¾ mils, a preferred thickness being about 0.7 mil, by any conventional method.

The exposure and fixation procedures are similar to those given above for Example I. The development temperature for synthetic vehicles of the above type are somewhat lower, around 180° F.

It should be understood that the present disclosure is for the purpose of illustration only and that this invention includes all modifications and equivalents which fall within the scope of the appended claims.

I claim:

1. A material capable of furnishing a record solely in the form of a distribution pattern of radiation scattering discontinuities formed within an otherwise substantially homogeneous vehicle, said material comprising a supporting film of polyethylene terephthalate having a surface coating of dry, water-resistant, non-hygroscopic thermoplastic vinylidene chloride polymer, said polymer having a light-decomposable, solid diazonium compound substantially uniformly dispersed therein as the sole image producing agent, said decomposable agent itself being non-reactive to said polymer and upon exposure to light decomposing into products which are also chemically non-reactive to said polymer and which upon warming

are volatile to form said radiation scattering discontinuities only in the light struck areas in said polymer to thereby furnish said record, said material being prepared by the steps of: preparing a uniform mixture of said polymer and diazonium compound in non-aqueous organic solvent, coating said mixture directly upon said supporting film and then drying the thus coated film to obtain said material.

2. The material of claim 1 wherein said coating is applied directly on said supporting film as a ketonic solution in the absence of water.

3. The material of claim 1 wherein said diazonium compound is p-N,N-dimethylaminobenzene diazonium zinc chloride.

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