

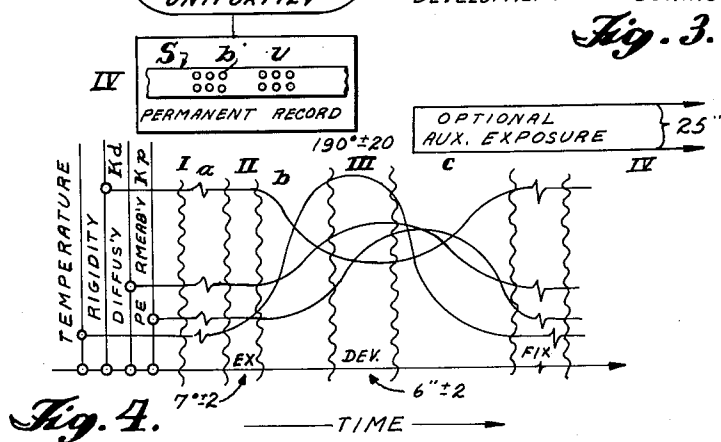
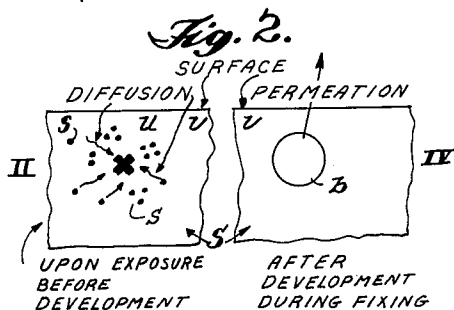
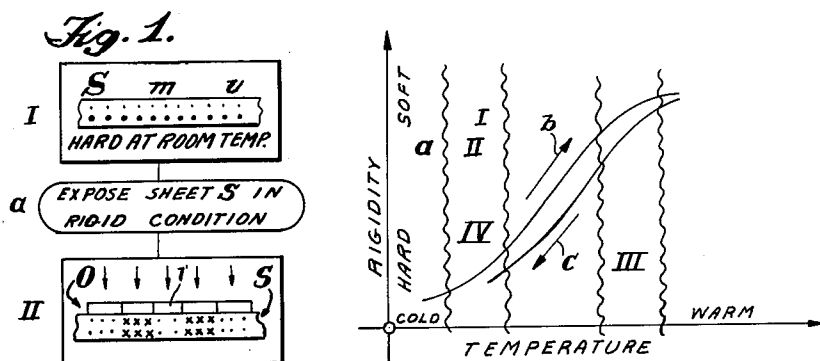
**May 1, 1962**

R. W. JAMES ET AL

**3,032,414**

## SYSTEM OF PHOTOGRAPHIC REPRODUCTION

Filed Nov. 19, 1956



INVENTOR

RAYMOND W. JAMES

RIENZI B. PARKER

BY *Cushman, Darby & Cushman*

**ATTORNEYS**

1

3,032,414

**SYSTEM OF PHOTOGRAPHIC REPRODUCTION**  
Raymond W. James, Lexington, and Rienzi B. Parker,  
Concord, Mass., assignors, by mesne assignments, to  
Kalvar Corporation, New Orleans, La., a corporation  
of Louisiana

Filed Nov. 19, 1956, Ser. No. 623,050  
9 Claims. (Cl. 96—91)

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. This application is a continuation-in-part of application Serial Number 380,855, filed September 17, 1953.

It is a principal object of the invention to provide photographic reproductions according to a technique which is inexpensive, extremely simple, and particularly reliable as to stability and independence from extraneous effects of the materials used, which permits satisfactory operation with a minimum of effort of unskilled labor and in minimum time, regardless of environmental conditions such as ambient moisture and temperature.

Another object is to provide a reproduction technique for offices, libraries, drafting rooms and similar establishments, which technique employs material that is comparatively inexpensive, stands up well through reasonably rough routine handling, produces exact copies, and is permanent and insensitive to deterioration prior to and after printing, especially as to moisture, to which other systems of this type are rather sensitive.

A further object is to provide such a technique which is completely independent of atmospheric humidity and ambient temperature, with the resultant advantages as to storing and processing of the initial material as well as the end product.

Additional objects are to provide a reproduction technique of the above type which is dry throughout, which is independent of water in any form or manner of occurrence and which does not require chemical treatment or rinsing baths, to provide such a technique which optionally permits the direct printing of either negative or positive copies with the same material, apparatus and general procedure, and to provide a technique which is insensitive to moisture within and outside of the material involved so that it can be exactly and positively predetermined independently from environment, mode of storage or preparation, and other circumstances dependent on necessarily more or less unskilled labor, thus providing a better end product without additional complications.

Photographic copying systems of the present type have heretofore been suggested and while some of these offer generally speaking many of the advantages inherent in this type of photography, they are in certain environments and under certain working conditions more or less impractical due to the fact that they employ organic colloid vehicles which are water sensitive and therefore subject to the effects of ambient moisture which cannot always be satisfactorily controlled. Attempts to use synthetic plastic materials instead of natural colloids were heretofore unsuccessful, apparently due to the failure of basing such a photographic system strictly upon clearly recognized requirements of photographic record formation of this type, rather than upon attempts to replace natural colloids with synthetics duplicating their properties.

According to the present invention in one of its aspects, raw stock for purposes of forming a photographic record in terms of substantially purely textural change of the materials, comprises a sheet or similar shape of water inert thermoplastic optically substantially homogeneous vehicle material (applied to a suitable support or self-sup-

2

porting) containing a sensitizing substance which is capable of generating gas upon exposure to radiation (such as visible or ultra violet light) which gas expands to form bubbles which cause the record defining textural change, this vehicle material having diffusivity and permeability properties which at a given exposure temperature below a given developing temperature and below the disintegrating temperature of the sensitizing substance promote formation of units of a true gas from the gas molecules or molecule groups (herein referred to as sources) generated by exposure and which at either temperature promote gas permeation gradually to liberate the record forming gas from the vehicle material, for fixing the record, and which have a rigidity which at the temperatures involved preserve the requisite physical stiffness.

In another aspect of the invention, the vehicle material and the sensitizer substance are soluble in different but miscible nonaqueous solvents, the sensitizer being molecularly or colloiddally dispersed in the vehicle.

In a further aspect, the raw stock according to the invention comprises a vehicle which is essentially composed of a binder and a modifier which mutually adjust the diffusivity, permeability and rigidity of the vehicle as a whole.

In an especially important practical embodiment of the invention, the vehicle is Saran, modified with Acryloid (both synthetic resins which will be more accurately identified hereinbelow) which are practically water inert but both soluble in nonaqueous solvents such as methyl ethyl ketone, and the sensitizer is a diazo compound which for compounding with the vehicle is dissolved in a substance which is miscible and compatible with the vehicle solvent, such as methanol if the Saran-Acryloid vehicle is dissolved in ketone.

Printing material according to the invention results upon exposure, development, and fixing as herein described, in a photographic record in terms of substantially purely textural change which comprises a sheet of thermoplastic vehicle containing record forming cavities or bubbles and essentially invisible decomposition products of a sensitizing substance capable of generating gas sources upon exposure to radiation, which vehicle is water inert and has diffusivity and permeability properties which at a given exposure temperature below a given developing temperature and below the disintegrating temperature of the sensitizing substance promote formation of gas units that effect such cavity formation, and the rigidity of the vehicle essentially preserving at such temperatures the record forming cavities or bubbles.

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, mode of operation and practical possibilities together with a description of several typical embodiments and examples illustrating its novel 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 material according to the invention;

FIG. 3 is a diagram illustrating diffusion events within material according to the invention, in a process according to FIG. 1; and

FIG. 4 is a diagram of the changes of temperature, plasticity, diffusivity, and permeability within the time cycle of a process according to FIG. 1.

## Process Prototype

The properties of printing material according to the invention depend mainly upon its use, and it can best

3

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 this material during such a process are illustrated in FIGS. 2, 3 and 4, and the process steps of the flow diagram and the corresponding portions of FIGS. 2, 3 and 4 are similarly labeled.

In block I of FIG. 1, sheet material according to the invention is indicated at S without support, but it will be understood that it can also be applied to conventional supports or to supports particularly modified and useful for purposes of the present invention such as will be especially referred to below.

This material S comprises a thermoplastic vehicle  $v$  with molecules or molecule groups  $m$  of sensitizing 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  $a$  in block II, the material S in that 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 sign, which term is herein used to describe the general gradation relation of original and copy as viewed in ordinary use; 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. This convention refers to the record pattern proper independently of the character of the support which for this purpose is assumed to be transparent.

A preferred embodiment employs a sensitizer ("Edwal" or "Ringwood," see below) which is essentially sensitive to radiation within the 300 and 420 millimicron range which permits handling in ordinary room 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 according to the invention 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 original O is thus copied with opposite sign in terms of invisible units  $u$  constituting a latent record.

As indicated at  $b$  the vehicle  $v$  of the sheet S is then softened by raising its temperature, which induces record development by expansion of the gas units  $u$  into gas bubbles  $b$ . At III, the sheet S now contains a developed record, corresponding to that of the original O, in terms of visible bubbles containing gas. Sensitizer molecules  $m$  remain in the unexposed portions.

The heating of sheets S 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, the following procedure is especially certain. As indicated at  $c$ , the sheet S is again hardened by cooling it, thus inhibiting further expansion of the bubbles. A uniform exposure is then applied and the gas which develops during such exposure is allowed to permeate through the vehicle  $v$  into the atmosphere. The record defining bubbles  $b$  solely remain, as shown at IV of FIG. 1. In many instances it is quite satisfactory to store the copies at room temperature in subdued light. The remaining sensitizer then generates gas gradually which permeates from the vehicle without forming bubbles.

#### *The Printing Material in General*

The usefulness of copying material according to the

4

invention, in processes of the general type indicated by the above typical example, depends on the mutually complementary properties of the vehicle material, the sensitizer substance, and the support if such is used.

The vehicle in addition to being essentially inert to environmental influences especially moisture and heat, must be capable of receiving in dispersion of controllable fineness and uniformity a sensitizer furnishing upon irradiation a gas compatible with those physical properties of the vehicle which are primarily desirable with a view to the formation of a permanent record of desirable contrast and definition, by way of a minimum amount of easily applied control operations. The sensitizer, in addition of being compatible with the vehicle with regard to incorporation and record formation therein should have suitable sensitivity and gas generating properties. The support will be selected for optimum presentation of the textural record under given viewing conditions.

The vehicle is, for purposes of the invention, primarily selected with a view to absolute independence from moisture and temperature, whether due to climate or accidental application. Vehicles according to the invention are essentially inert to wear. They do not dissolve or swell in water nor are they subject to water inclusion, although they may so to speak constitute a passageway for water in the purely mechanical sense comparable to a sieve but without effect upon the structure and molecular pattern of the vehicle. As well known, this moisture vapor penetrability of hydrophobic plastic material, although small, is nevertheless separately detectable and measurable as clearly distinct from the high degree of moisture sorption with the consequent effect on the physical properties of certain plastics which, accordingly, are unsuitable for purposes of the invention.

The vehicles according to the invention are self-supporting or applicable to separate supports with preservation of all advantages calling for such supports.

The operating temperatures of these vehicles are such that as to variety, range and general level they are 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 and the vehicle has at that temperature properties especially well suited for the formation of the visible bubble record.

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 bubbles. The permeation of gas is its transfer by diffusion through the vehicle from a space of higher pressure such as the bubbles, 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 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 is one of the factors that control diffusion and permeation of the gas; it also determines the macroscopic mechanical properties of the record sheet.

The above terms are herein used in accordance with commonly accepted concepts, as follows.

Diffusion is the spontaneous redistribution of particles

in solution to establish equalization of a physical state; in the present instance, diffusion towards centers of nucleation probably establishes gas units at such centers as will be discussed below. Diffusivity is the quantity of a substance passing normally through a unit area per unit time per unit gradient of volume concentration; it can be expressed in terms of a diffusivity constant.

Permeation is the passing of a gas through a boundary of a body. Permeability is the rate of permeation of a gas under standard conditions. Permeability is usually expressed in terms of a permeability constant which, as mentioned above, is approximately proportionate to the diffusivity constant, so that both permeability and diffusivity can be evaluated by way of a permeability constant for each vehicle material.

It was originally thought that, while diffusivity co-determines permeability, the dependency of the latter thereon is not herein of primary importance because the adjustment of permeability is mainly qualitative and can be sufficiently controlled for purposes of the invention, that is for removal of gas by permeation from the vehicle into atmosphere, by temperature and time adjustment. On the other hand, it is now known that diffusivity is quantitatively instrumental regarding the formation, distribution and size of the gas sources and hence of the record defining bubbles, or holes after the gas has permeated the rigid vehicle upon fixation. Furthermore, the vehicle diffusivity was found to be definitely characterized by its permeability. Thus it is now recognized that, while both diffusivity and permeability are important factors, the permeability alone suffices as a primary characteristic of vehicles suitable for purposes of the invention. Therefore, instead of saying that diffusivity should be treated as a separately controlled phenomenon rather than as one of the factors that define permeability, it can now be said that the two phenomena, diffusivity and permeability, are directly related so that a single parameter suffices to define the vehicle in its dependency upon both.

Diffusivity can be mathematically defined as a function of temperature and material constants; and, in accordance with the above concepts, permeability is a function of diffusivity and particularly for the purposes of the invention, permeability is proportionate to the diffusivity. 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.

The diffusion within the vehicle substance proper, by which the gas molecules move through the vehicle body, is here of importance beyond its significance as a stage in the over-all permeation process, because it enables units of true gas to be formed before any permeation takes place, which gas units are the primary record elements. They represent bodies of a true gas which expands upon relaxation of the vehicle to form bubbles whose size is controlled by the adjustment of the molecular flow of the vehicle, in addition to control of the initial amount of gas obtained upon exposure of the sensitizer to radiation.

While any arbitrary units of diffusivity and permeability serve the purpose of explaining the essential qualities of vehicles that are suitable for purposes of the invention, it has been found that the scientifically precise concept "permeability constant" is better suited for defining these qualities. The permeability constant, as herein used, is the number of cubic centimeters of gas transmitted by the unit area of one square centimeter during one second at constant, such as room, temperature, when the pressure gradient is one centimeter of mercury per centimeter of the thickness of a vehicle layer of a given material. This quantity is subject to direct measurement in absolute physical units. The choice of units is arbitrary, but these units are widely used in this country. This definition of permeability is quite different from that appearing in some British publications where the transport rate under any set of conditions is referred to as the "perme-

ability." By this latter definition, permeability depends on the particular conditions such as of pressure difference and vehicle layer thickness.

The above mentioned diffusivity constant which is for present purposes approximately proportionate to the permeability constant might possibly be more desirable from the standpoint of theory, but the permeability constant appears to be an equally good index for present purposes, especially since it lends itself fairly easily to exact measurement which is not generally true of the diffusivity constant.

FIG. 3 illustrates these concepts, but it should be kept in mind that it can only give a rough and incomplete model of the rather complicated phenomena involved and herein discussed only so far as they are essential for purposes of the invention. In FIG. 2, the vehicle *v* of a sheet *S* is at II (compare FIG. 1) shown during exposure, when the gas molecules, or groups thereof herein referred to as gas sources *s*, diffuse within the rigid vehicle to form units *u*. At IV the vehicle *v* is shown after development and during fixing, when the gas units have expanded to form bubbles *b*. The vehicle is here again rigid and the gas escapes from bubbles *b* by permeation into the atmosphere.

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' laws relating to the volume to pressure and temperature respectively, after the release, from the sensitizer, 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. 2. If these sources were trapped within the vehicle upon the release by photolysis, they could not form the smallest units with the above characteristics of a true gas. The sources and units constitute an invisible latent record of the image defining radiation pattern as determined by original *O* (FIG. 1), which causes their release from the sensitizer within the vehicle. The gas contents of the units varies to a degree which can be controlled by way of the diffusivity. The upper limit of diffusion is determined by the spatial resolution required in the finished product and hence by the size of the ultimate record forming bubbles or holes. For example, a resolution of 1,000 lines per inch requires bubbles not appreciably larger than approximately 10 microns in diameter, which maximum corresponds to a line about two bubbles wide. Accordingly for purposes requiring resolution of this fineness, the diffusion of the gas has to be so adjusted that units containing substantially more than the requisite amount of gas do not occur. Furthermore, the diffusion has to be so regulated that the gas does not wander from the exposed areas into unexposed areas where it might later cause general background fog.

In addition to considerations of exposure and development, as above discussed, those relating to record permanency are of primary importance. These are herein referred to as fixation in conformity with general photographic usage, although they are unique in the present context.

Fixation has the purpose of making the record proper stable and permanent in general use, preventing its disappearance or reduction in contrast or sharpness subsequent to development; it must also be stable against fogging or accidental re-exposure to more than average light intensities and it must further be mechanically stable that is sufficiently hard to withstand ordinary handling including damage by scratching, or softening under the heat of a projector lamp. Fixation is accomplished by so to speak freezing the bubble structure by making its walls sufficiently rigid so that, even though the gas subsequently permeates the vehicle body between the bubble and the outside, there remains a light scattering structure which is mechanically strong enough to maintain

itself against ordinary use while defining the intended record pattern. As mentioned above, a preferred way of fixing is to release the gas from the non-exposed sensitizer molecules without permitting it to form bubbles and thereupon permitting it to escape completely so that bubbles cannot form thereafter. In many instances the steps of fixating exposure and permeation can be combined by storing the developed material for a few hours at room temperature in subdued light.

The requisite conditions of increased plastic flow during development are brought about by heating of the thermoplastic vehicle by conduction, convection or radiation. The physical means for applying heat can be quite simple which is a primary advantage of the present process. FIG. 2 illustrates this operation. The low temperature range marked I, II, IV represents a rigid yet permeable phase which is the normal condition, also employed during exposure. In range III the vehicle is relaxed permitting the bubble expansion during development, which is interrupted by cooling when the desired record 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 FIGS. 1 and 3, regions I and II prevailing during exposure, region III during development, and region IV during fixation and afterwards.

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

Thermoplastic vehicle material which is suitable for the above purposes can be selected from a variety of classes, regardless of chemical origin, the requisite properties being purely of a physical nature. Primarily the vehicle must be water inert and suitable for incorporation of the sensitizer either mechanically such as by way of a ball mill, or by way of solvents other than water. According to the invention the latter can be done either by choosing a sensitizer and a vehicle which in addition to having the requisite photographic properties, are soluble in the same agent, or by selecting a vehicle and a sensitizer which are soluble in different but compatible solvents; in other words the common solvent can be a mixture of compatible solvents for vehicle and sensitizer respectively.

Recapitulating, the vehicle must be self-supporting or applicable to a suitable support, it must have diffusivity and permeability characteristics providing optimum photographic quality, as above described, and operational control by means of temperature adjustment within easily controlled limits below the decomposition temperature of the sensitizer and providing optimum relaxation during development, and finally its rigidity under normal ambient temperature condition must provide the requisite permeability.

It was found that certain vehicle materials are immediately available for purposes of the invention, such as polystyrene, polyvinyl chloride, and polyvinylidene chloride under certain conditions to be set forth hereinbelow.

Unmodified ethyl cellulose, while it is of very limited usefulness for practical purposes, has been proposed as a standard representing the upper limit of permeability in accordance with the present invention, but it was later found that unmodified polystyrene is better suited for that purpose since it is useful for a wider range of practical applications.

In addition, the following copolymers were found to be definitely useful for some if not all purposes to which scatter photographs can be put, namely copolymers of vinyl chloride and vinylidene chloride, vinyl chloride and acrylonitrile, styrene and acrylonitrile, acrylonitrile and 1,1 difluoroethylene, vinylidene chloride, and acrylic acid, vinyl acetate and vinylidene cyanide, vinyl chloride and acrylic acid, vinyl chloride and methyl acrylate, vinylidene chloride and ethyl acrylate, vinylidene chlorofluoride and

acrylonitrile, vinylidene chloride and methyl methacrylate, vinyl acetate and vinylidene chloride, vinyl alcohol and vinylidene chloride, vinyl chloride and diethyl maleate, vinyl chloride and vinyl acetate.

Materials available directly for purposes of vehicles often have one or more physical characteristics which do not satisfy the requirements of the present invention. It is therefore preferred, in an important aspect of the invention, to modify vehicle material which is not directly suitable for optimum results by auxiliary admixtures, herein referred to as modifiers. Also, some plastics are not operative to the optimum degree although sufficient for certain purposes. Such vehicle material can be materially improved for optimum performance by the use of modifiers according to the invention.

It is possible to use a vehicle plastic which has the proper rigidity-temperature relation but is not quite satisfactory concerning diffusivity and permeability, and to correct the latter defect by adding a modifier for permeability adjustment. It is also feasible, instead of using a modifier for diffusivity adjustment to select a vehicle with correct diffusivity but unsuitable, such as low, rigidity, and to add a modifier for correcting the rigidity. As a third, and indeed especially desirable embodiment we select, according to an important aspect of the invention, a vehicle plastic of good general physical characteristics but having a rigidity as well as diffusivity characteristics which are not quite suitable for the invention, which latter we correct by means of a modifier which adjusts diffusivity and permeability as well as rigidity. Separate rigidity and diffusivity modifiers can be used.

In a preferred embodiment which will be described more in detail hereinbelow, a vehicle is used which has a low diffusivity as well as rigidity, and both are increased by a modifier, so to speak a negative plasticizer or hardener and a positive permeabilizer, two functions which are usually regarded as contradictory.

In another likewise workable embodiment, a vehicle is used which is comparatively hard and too permeable and which is therefore compounded with a modifier that decreases its permeability.

Materials which were found suitable for purposes of the present invention, as vehicles requiring in most instances some modifier, are polyvinyl butyral, Vistanex (polyisobutylene), Koroseal (polyvinyl chloride), and Saran (polyvinylidene chloride).

Ethyl cellulose has the highest allowable permeability, that is a permeability which permits bubble formation prior to escape of the gas before it has a chance to form bubbles. Thus this material can be utilized as a limiting standard as mentioned above, but it will be understood that it is vastly improved by adding a modifier which permits a practical time interval between exposure and development. As mentioned above, polystyrene material was found to be better suited for this purpose.

As mentioned above, many of the vehicle materials which are listed above as suitable without modifier, can be considerably improved for particular purposes by compounding with a modifier. This is for example true of the polyvinylidene chloride-acrylonitrile copolymer which is described hereinbelow within the framework of Example I.

Needless to say, the modifier concept according to the invention permits a fairly wide choice among vehicle material available for individual purposes as defined by general requirements for printing material and records in any particular instance.

The herein listed materials in so far as they are suitable for purposes of the present invention, must have, as a basic property determining their usefulness for that purpose, a permeability constant, as above defined, that is not greater than

$$P_{\max} = 8 \times 10^{-10} [\text{cm.}^3 \text{ cm.}^{-2} \text{ sec.}^{-1} (\text{cm. Hg./cm.})^{-1}]$$

wherein the bracketed dimension conforms to the above

definition of the permeability constant. This condition must be satisfied by the unmodified vehicle if used as such, or by the vehicle with a modifier admixture added to a binder.

While the above upper limit of  $P=8 \times 10^{-10}$  is fairly critical, a lower limit is not equally well defined or critical; however materials with constants below  $P_{\min}=8.6 \times 10^{-16}$  in most instances will be unsatisfactory.

The above values for P are referred to temperatures of approximately 30° C. They are also referred to nitrogen, the gas which is at the present time most practical for purposes of scatter photography, although other gases such as CO<sub>2</sub> have been used. These P values for nitrogen diffusion however are, within the range specified, sufficiently close to those for other gases so that they serve satisfactorily for selecting a proper unmodified vehicle or for compounding with a modifier a vehicle that in itself does not conform to this permeability requirement.

The above permeability limits determine usefulness mainly as to photographic sensitivity and resolution. In general, these improve as the permeability is reduced. Furthermore copies which are thermally stable at ordinary storage temperatures are obtainable within these permeability ranges. If it is desired to destroy the sensitizing material that remains after the record exposure proper, by rendering it insensitive, exposure to the necessary light within an interval of a few seconds may result in fogging. This can be prevented by a modifier which raises the permeability, permitting gas to escape. It will now be evident that it is also possible to achieve the same effect by the choice of a vehicle material of somewhat higher permeability. For example, with vinyl-type vehicles such as that of Example 1 hereinbelow, permeabilities of about  $2 \times 10^{-12}$  permit rapid fixing, at the same time retaining good resolution and speed. In addition to the increase of permeability with a modifier to permit fixing, an alternate type of modification is possible. A given resin may have permeability higher than the upper limit of the operating range. This can be brought within the operating range by adding a modifier of low permeability. Thus the modifier is a method of adjusting the over-all permeability to some desired value.

The hardness of the vehicle polymer is not very critical with regard to permanence, since the net forces acting to destroy the record are weak if it is not subject to high pressure and temperature simultaneously.

Vehicle materials according to the invention are further characterized, in purely physical, structural, terms, as primarily highly linear and saturated hydrocarbon chains essentially without cross links, such as obtained by polymerization of monomers with substituent groups preferably of small dimensions, made up of one or two atoms, and in many cases of a moderately electronegative character, imparting the polymer with a certain amount of polarity, or strong interchain cohesion, favoring close molecular fit and crystallinity, with closely adjacent molecule portions forming randomly distributed elementary structures interspersed with randomly distributed areas of lower coherence. These low cohesion areas are believed to constitute, or at least to favor the formation of, nucleating areas where the above described gas units tend to form. Many of the usable materials result from the interpolymerization of two ethylenic monomers resulting in the desirable properties of solubility, and color stability.

The sensitizer must be capable of dispersion within the vehicle sufficiently fine for purposes of the required definition as further controlled by the above discussed diffusivity and rigidity characteristics of the vehicle. The diffusivity depends a good deal on the distribution of the sensitizer and this distribution again depends largely on the manner of incorporating the sensitizer. Furthermore the pressure under which the gas is released during exposure is a function of the concentration of the sensitizer, of its photolytic efficiency upon irradiation, and upon the

rigidity of the vehicle against which the gas must expand. Materials complying with these requirements can be compounded according to the invention by means of the above outlined modifier principle.

Compounds of the diazo type which upon irradiation liberate nitrogen were found to be especially suitable, but other compounds for example of the type which liberate carbon oxides can be used.

Among the sensitizing substances which liberate nitrogen units upon irradiation, para-diazo dimethyl aniline zinc chloride was found to be especially valuable, but the following substances were also found to be practical:

p-Diazo diphenylamine sulfate, p-diazo diethylaniline zinc chloride, p-diazo ethyl hydroxyethylaniline zinc chloride, p-diazo ethyl methyl aniline zinc chloride, p-diazo diethyl methyl aniline zinc chloride, p-diazo ethyl hydroxyethylaniline zinc chloride, 1 diazo-2 oxy naphthalene-4 sulfonate, d-diethyl amino benzene diazonium chloride ZnCl<sub>2</sub>, 4-benzoylamino-2-5-diethoxy benzene diazonium chloride, p-chlorobenzene-sulfonate of 4-diazo-1-cyclohexylaniline, p-chlorobenzene-sulfonate of 4-diazo-2-methoxy-1-cyclo-hexylamino benzene, tin chloride double salt of 4-N-methylcyclohexylamino-benzene diazonium chloride, p-acetamino benzene diazonium chloride, 4-dimethylamino benzene diazonium chloride, 3-methyl-4-diethyl amino benzene diazonium chloride, 4-morpholino benzene diazonium chloride, 4-piperidyl 2-5-diethoxy benzene diazonium chloride, 1-dimethyl amino naphthalene-4-diazonium chloride, 4-phenyl amino diazo benzene diazonium chloride.

The support can be of any suitable material which will be transparent if the exposure takes place therethrough or if the reproduction is intended to be a diapositive. Glass, ethyl cellulose, the plastic available under the trade designation "Mylar" (a polymer resulting from the condensation of terephthalic acid and a glycol), and similar substances are satisfactory provided they withstand the operational temperatures required and are relatively free from plasticizers which tend to wander into layers on the support. Cellulose acetate supports which, generally speaking, are undesirable because of containing wandering plasticizers, can be used if a suitable barrier layer is interposed between such a support and the layer thereon.

Opaque supports will generally be flexible such as paper or synthetic sheet material. These supports can be of any desirable color, but black supports were found particularly suitable for certain purposes. The bubble record appears white on such black supports, constituting a copy of the opposite sign, while the same record on a transparent support furnishes for diapositive purposes a copy of the same sign. Generally speaking the diffusing bubble record will appear light or dark depending on the transmission-reflection characteristics of the backing or support, and this must be taken into consideration in describing the photographic sign of the record.

By using suitable modifiers which permit considerable leeway in compounding materials of optimum photographic qualities, vehicle materials can be selected which are self-supporting.

Ethyl cellulose is a preferred support, and the above listed polystyrene in thickness of 1/2 to 3/4 mils, compounded with a suitable modifier, was found very satisfactory in sheets without support.

#### Specific Embodiments

*Example I.*—The vehicle material in this example (herein also referred to as binder) is a synthetic resin which has good general properties but has low permeability to nitrogen and hence could not be rapidly fixed if used alone. It is modified with another synthetic resin which affects both diffusivity and rigidity, acting as mentioned above, as a negative plasticizer and positive permeabilizer. The

exact formula for a sensitized vehicle of this type is as follows:

| Function        | Component                   | Parts by Weight |
|-----------------|-----------------------------|-----------------|
| Vehicle.....    | Saran F-120 (200 cps.)..... | 17.0            |
| Modifier.....   | Acryloid A101.....          | 3.0             |
| Sensitizer..... | Edwal Compound #8.....      | 1.2             |
| Solvent.....    | Methyl Ethyl Ketone.....    | 60.0            |
| Solvent.....    | Methyl Alcohol.....         | 12.0            |

Saran F120 is a vinyl type resin and described as a copolymer of vinylidene chloride and acrylonitrile.

Acryloid A101 is a polymethyl methacrylate as a 40% solution in methyl ethyl ketone. The weight given above is the calculated amount of the resin only.

Edwal Compound #8 is p-diazodimethylaniline zinc chloride.

The methyl alcohol is warmed to approximately 50° C. and the Edwal Compound stirred in. This solution is then diluted with 5 cc. of the 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 can be cast on an ethyl cellulose film such as used for photographic purposes, to a thickness of about 0.7 mil, using a conventional doctor blade. It is then dried to evaporate the solvent, which takes about 30 minutes at approximately 95° C. The printing material is then ready for use.

This vehicle can also be applied to opaque supports such as paper. In an especially useful embodiment, the vehicle as above compounded with modifier and sensitizer is coated on a black hard surface paper of the type available under the trade designation "Champion Kromekote Black" from the Champion Paper and Fiber Co. To this paper is first applied a subcoating of 0.25 mil ethyl cellulose in order to prevent the solvent from picking up color from the paper. The vehicle solution is again applied with a doctor, to a thickness of about 0.5 to 0.7 mil.

Instead of applying this vehicle to transparent or opaque, more or less permeable supports, it can be used in unsupported sheet form, rolled to a thickness of about 3 to 5 mils.

The exposure, development and fixing follows, generally speaking, the prototype outlined with reference to FIG. 1, but differs somewhat depending upon the support, as follows.

This material in unsupported sheets or applied to transparent, especially celluloid supports is exposed in direct contact with the original (compare FIG. 1) for about eight seconds at a distance of about ten inches from a standard B-H6 mercury lamp; this exposure can serve as a standard for other modes of printing.

Development is for example by confinement for about seven seconds between two steel plates heated to about 190° F. It is satisfactory to heat one plate electrically, its temperature being thermostatically maintained.

If this material is coated on opaque material such as the above described paper, contact exposure for five seconds about four inches from a B-H6 lamp is satisfactory. The development of such paper stock requires somewhat less time and temperature, about five seconds at 180° F. Stock of this type, namely coated on a less permeable support, requires a definite fixing procedure in order to prevent secondary development upon exposure to fairly intense radiation such as sunlight or the lamp of a viewer. Following development and cooling of such material it is re-exposed under the B-H6 mercury lamp for about 25 seconds at a distance of about two feet, depending somewhat on the thickness of the film. The material is then stored in a cool place for about an hour which allows the gas to permeate to the atmosphere, completing the fixing.

FIG. 4 illustrates the above described printing techniques indicating the entire cycle from the stored raw stock to the finished permanent record. The optional definite fixing step is likewise indicated. In view of the above explanations of FIG. 1 and of the properties of the material according to the invention, FIG. 4 is self-explanatory. It shows the interrelation of temperature (T°), rigidity (relative plasticity Pr), diffusivity (velocity factor Kd) and permeability (flow factor Kp) during the cycle; the temperature and time values are indicated for the case of Example I. It will be understood that these vary considerably depending on the material and working conditions selected for which they have to be experimentally checked, as customary in this art.

**Example II.**—In the above formula, Example I, the Edwal Compound is replaced by 2 parts by weight of the methanol soluble diazo compound namely, p-diazodiethyl-aniline zinc chloride, available under the trade designation "Sensitizer No. 38," from the Fairmount Chemical Co., Inc., of Newark, New Jersey. Since this sensitizer is more easily soluble in alcohol, the amount of methyl alcohol in the formula of Example I can be reduced to 6.0 per weight.

The compounding and use is essentially the same as above described for Example I.

**Example III.**—In this example a different type of vehicle is compounded with appropriate modifier, as follows:

| Function        | Component                | Parts by Weight |
|-----------------|--------------------------|-----------------|
| Vehicle.....    | Lustrex 15.....          | 75.0            |
| Modifier.....   | Arochlor 5460.....       | 25.0            |
| Sensitizer..... | Edwal Compound #8.....   | 10.0            |
| Solvent.....    | Methyl Ethyl Ketone..... | 400.0           |
| Solvent.....    | Methyl Alcohol.....      | 80.0            |

Lustrex 15 is a polystyrene.

Arochlor 5460 is a chlorinated polyphenyl.

This vehicle, namely Lustrex 15, is comparatively hard and too permeable; the Arochlor 5460 modifier decreases its permeability.

The coating of this compound and the use of the printing material are essentially as described for Example I.

**Example IV.**—In this example a vehicle is used which does not require a modifier. It is compounded as follows:

| Function        | Component                | Parts by Weight |
|-----------------|--------------------------|-----------------|
| Vehicle.....    | VAGH.....                | 14.0            |
| Sensitizer..... | Fairmont #38.....        | 1.4             |
| Solvent.....    | Methyl Ethyl Ketone..... | 40.0            |
| Solvent.....    | Methanol.....            | 12.0            |

VAGH is a copolymer of vinyl chloride and vinyl acetate.

The vehicle, namely the VAGH compound, is dissolved in the methyl ethyl ketone and the sensitizer added in the alcohol solution described above. The composition can be handled and coated as above described for Examples I to III.

The use of printing material made in this manner is similar to that in Example I; it will be understood however that each material may require individual, slight modification of treatment. As in all photographic techniques, a certain amount of experimentation in this respect is unavoidable.

**Example V.**—The vehicle is another unmodified copolymer compounded with a diazo sensitizer as follows:

| Function        | Component     | Parts by Weight |
|-----------------|---------------|-----------------|
| Vehicle.....    | Dynel.....    | 10              |
| Sensitizer..... | Edwal #8..... | 1               |
| Solvent.....    | Acetone.....  | 57              |
| Solvent.....    | Methanol..... | 8               |

Dynel is a vinyl-chloride-acrylonitrile copolymer.

The sensitizer is identified above, under Example I.

The resin is added to acetone with agitation. The sensitizer, dissolved in alcohol at 40° C., is added while stirring. The material was coated as described for Example V.

**Example VI.**—This embodiment of the invention is essentially similar to that of Example I, but incorporates certain optional improvements which render it especially versatile and provide, if desired, superior photographic qualities.

The components are the same as in Example I, with the difference that 2 parts by weight of the Edwal Compound #8 are used instead of 1.2 parts. The compounding of the vehicle binder with its modifier and with the sensitizer is likewise the same as in Example I.

The above described composition is cast to a thickness of about 0.5 mil on a transparent film made of the reaction product of ethylene glycol and terephthalic acid which produces a polyester film marketed under the trade name "Mylar." The casting and drying procedure is otherwise as described for Example I.

This material yields particularly satisfactory copies if continuously exposed in contact with the original such as a microfilm on a translucent transport cylinder of about 4" diameter, at a printing rate of about 5 to 10 feet per minute. The continuous printer has as a light source preferably two General Electric Co. 100 watt mercury lamps mounted parallel to the axis of the cylinder. While this printing procedure furnishes good reproductions, the definition is considerably improved by keeping the exposure arrangement at room temperature, for example by forcing air therethrough by means of a fan.

The development can be carried out continuously on a heated roller. In accordance with an improved technique, unexpectedly excellent results are obtained by developing at comparatively elevated temperatures, such as 250° F. for two to three seconds.

Fixation can be satisfactorily accomplished by exposure to a light source similar to that used for printing, followed by a waiting period of about one hour to allow complete gas permeation from the interior of the vehicle.

The prints made according to the above examples can be practically instantaneously fixed by uniform exposure to intense light.

**Example VII.**—The vehicle is an unmodified copolymer compounded with a methanol soluble diazo compound, as follows:

| Function        | Component                      | Parts by Weight |
|-----------------|--------------------------------|-----------------|
| Vehicle.....    | Geon Resin #222.....           | 15              |
| Sensitizer..... | Sensitizer #88 (Fairmont)..... | 1               |
| Solvent.....    | Methyl Ethyl Ketone.....       | 37              |
| Solvent.....    | Methyl Alcohol.....            | 9               |

Geon Resin #222 is a vinyl-vinylidene chloride copolymer; it is described as an extension of the well known "Geon Resin #200" series, having a higher vinylidene chloride content. Its permeability constant is approximately  $5 \times 10^{-14}$ .

The sensitizer is identified above, under Example II.

The Geon resin is added to the methyl ethyl ketone with continual agitation. When the resin is in solution the sensitizer, which has first been dissolved in methyl alcohol of 40° C. is added while stirring is continued. After stirring for a few minutes the material was coated on strip material using a wire wound bar as a coating blade. The coatings are dried for 45 minutes at 180° F.

**Example VIII.**—The vehicle is an unmodified Saran, compounded with a diazo sensitizer, as follows:

| Function        | Component                | Parts by Weight |
|-----------------|--------------------------|-----------------|
| Vehicle.....    | Saran F-120.....         | 10.0            |
| Sensitizer..... | Edwal Compound #8.....   | 1.0             |
| Solvent.....    | Methyl Ethyl Ketone..... | 30.0            |
| Solvent.....    | Methyl Alcohol.....      | 8.0             |

The Saran here in use is the same as identified above for Example I.

The Saran used without modifier was found to have a permeability constant of about  $8.6 \times 10^{-14}$  measured in accordance to the practice set forth above.

The sensitizer is identified above, under Example I.

The resin and the sensitizer are compounded as described above Example I.

This copying material is useful for many purposes, where instantaneous complete clearing by ambient light is not essential. It gives good definition, and often even better definition than material according to Example I, and can be permanently fixed or "cleared" by gradual diffusion of the nitrogen that is generated under overall exposure to diffused light of lower than average intensity, such as at daylight in an average room with drawn shutters.

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.

We claim:

1. A method of preparing 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 being in the form of a dry, water-resistant non-hygroscopic film having a permeability constant for nitrogen within the range of  $8.6 \times 10^{-16}$  and  $8 \times 10^{-10}$ , said constant being the number of cubic centimeters of nitrogen transmitted at 30° C., by an area of one square centimeter in one second when the pressure gradient is one centimeter of mercury per one centimeter of transmission thickness, the continuous phase of said film being essentially a synthetic, water-insoluble, non-hygroscopic, non-water swelling, highly linear thermoplastic polymer selected from the group consisting of homopolymers of styrene, homopolymers of vinyl chloride, homopolymers of vinylidene chloride, copolymers of vinyl chloride with a different vinyl monomer and copolymers of vinylidene chloride with a vinyl monomer and a substantially non-volatile organic material which is compatible with said polymer so that said film is optically homogeneous, said organic material being present in said film only to the extent necessary to give said film the aforesaid permeability constant for nitrogen and a light decomposable solid agent substantially uniformly dispersed therein as the sole essential image producing agent, said decomposable agent itself being non-reactive to said vehicle and upon exposure to light decomposing into products which are also chemically non-reactive to said vehicle and which solely 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 organic material being other than the selected polymer and light decomposable solid agent, said method comprising the steps of combining said components polymer, agent and any organic material necessary to give the indicated permeability in non-aqueous organic solvent for said components to form a uniform, essentially water-free mixture thereof and then forming said record material with the indicated permeability and composition.

2. A method of preparing a material as described in claim 1 wherein said polymer is one of the indicated vinylidene chloride polymers and it contains polymethylmethacrylate as said organic material, and said light decomposable agent is a diazo compound, said method

comprising the steps of: dissolving said diazo compound by stirring it into heated methyl alcohol; diluting said solution by adding methyl ethyl ketone; dissolving said vinylidene chloride polymer and said polymethyl methacrylate in methyl ethyl ketone; heating said methyl ethyl ketone solution; and adding thereto said methyl alcohol and methyl ethyl ketone solution of said diazo compound.

3. A method of preparing a material as described in claim 1 wherein said polymer is a copolymer of vinylidene chloride and acrylonitrile, containing polymethyl methacrylate as said organic material, and said light decomposable agent is a diazo dimethylaniline metal halide, said method comprising the steps of dissolving approximately 1.2 to 2 parts by weight of said diazomethylaniline metal halide by stirring it into approximately 12 parts by weight of methyl alcohol heated to approximately 50° C.; diluting said solution by adding approximately 5 cc. of methyl ethyl ketone; dissolving approximately 17 parts by weight of said copolymer of vinylidene chloride and acrylonitrile and approximately 3 parts by weight of said polymethyl methacrylate in approximately 55 parts by weight of methyl ethyl ketone; heating said methyl ethyl ketone solution to approximately 50° C.; and slowly adding thereto while stirring, said methyl alcohol and methyl ethyl ketone solution of said diazo methylaniline metal halide.

4. A method as claimed in claim 1 wherein said polymer is dissolved in a ketone and the decomposable agent is dissolved in a lower aliphatic alcohol miscible with said ketone.

5. Material for forming a photographic record in terms of substantially purely textural change of said material, comprising as a record vehicle a layer containing as a binder a substantially water inert vinylidene chloride resin and as a modifier a substantially smaller amount of polymethyl methacrylate, and dispersed in said vehicle as a sensitizer a diazo compound capable of generating nitrogen upon exposure to radiation which nitrogen is capable of expanding to form bubbles which cause said textural change, said vehicle being compounded with said sensitizer in miscible organic solvents for both vehicle and sensitizer, in a proportion such that the vehicle has a diffusivity which at a given exposure temperature below a given developing temperature and below the disintegrating temperature of said diazo compound establishes nitrogen sources, upon exposure to said radiation, a rigidity which at said developing temperature limits nitrogen expansion beyond formation of said bubbles to a record preserving degree, and a permeability which at either temperature gradually liberates said nitrogen from said vehicle, for fixing the record.

6. Material according to claim 5 wherein said vehicle layer comprises as said binder approximately 17 parts by weight of a copolymer of vinylidene chloride and acrylonitrile, and as said modifier, 3 parts of polymethyl methacrylate.

7. Material for forming a photographic record in terms of substantially purely textural change of said material, comprising as a record vehicle a layer containing as a binder a copolymer of vinylidene chloride and acrylonitrile and as a modifier a polymethyl methacrylate, and containing dispersed in said vehicle as a sensitizer a diazo-dimethylaniline metal halide capable of generating nitrogen upon exposure to radiation, which nitrogen is capable of expanding to form bubbles which cause said textural change, said vehicle being compounded with said sensitizer as solutions of said binder and said modifier in methyl ethyl ketone and of said sensitizer in methyl alcohol, in a proportion such that the vehicle has a diffusivity which at a given exposure temperature below a given developing temperature and below the disintegrating temperature of said sensitizer establishes nitrogen sources upon exposure to said radiation, a rigidity which at said developing temperature limits nitrogen expansion beyond formation of said bubble to a record preserving

degree, and a permeability which at either temperature gradually liberates said nitrogen from said vehicle, for fixing the record.

8. A record furnishing material capable of furnishing a record solely in the form of a distribution pattern of radiation scattering discontinuities formed within a vehicle which is optically substantially homogeneous, said material being in the form of a dry, water-resistant, non-hygroscopic film having a permeability constant for nitrogen within the range of  $8.6 \times 10^{-16}$  and  $8.6 \times 10^{-10}$ , said constant being the number of cubic centimeters of nitrogen transmitted at 30° C., by an area of one square centimeter in one second when the pressure gradient is one centimeter of mercury per one centimeter of transmission thickness, the continuous phase of said film being essentially a synthetic, water-insoluble, non-hygroscopic, non-water swelling, highly linear thermoplastic polymer selected from the group consisting of homopolymers of styrene, homopolymers of vinyl chloride, homopolymers of vinylidene chloride, copolymers of vinyl chloride with a different vinyl monomer and copolymers of vinylidene chloride with a vinyl monomer, and a substantially non-volatile, organic material which is compatible with said polymer so that said film is optically substantially homogeneous, said organic material being present in said film only to the extent necessary to give said film the aforesaid permeability constant for nitrogen, a light decomposable solid agent substantially uniformly dispersed in said film as the sole essential image producing agent, said decomposable agent itself being substantially non-reactive to said vehicle and upon exposure to light decomposing into products which are also chemically substantially non-reactive to said vehicle and which solely upon warming are volatile to form said radiation scattering discontinuities only in the light struck areas in said film having the indicated permeability to thereby furnish said record, said organic material being other than the selected polymer and light decomposable solid agent, said record furnishing material being obtained by combining the components polymer, agent and any necessary amount of said organic material in non-aqueous organic solvent for said components to form a uniform, essentially water-free mixture thereof and forming the record material therefrom with the indicated permeability and composition.

9. Record furnishing material according to claim 8 wherein said polymer is sufficient to give said permeability and said film is free from said organic material.

#### References Cited in the file of this patent

##### UNITED STATES PATENTS

|           |                     |               |
|-----------|---------------------|---------------|
| 2,318,352 | Alink .....         | May 4, 1943   |
| 2,405,523 | Sease et al. ....   | Aug. 6, 1946  |
| 2,501,874 | Peterson .....      | Mar. 28, 1950 |
| 2,613,149 | Unkauf .....        | Oct. 7, 1952  |
| 2,627,088 | Alles et al. ....   | Feb. 3, 1953  |
| 2,684,341 | Anspson et al. .... | July 20, 1954 |
| 2,699,392 | Herrick et al. .... | Jan. 11, 1955 |
| 2,703,756 | Herrick et al. .... | Mar. 8, 1955  |
| 2,709,654 | Guth .....          | May 31, 1955  |
| 2,712,996 | Elliott .....       | July 12, 1955 |
| 2,737,503 | Sprague et al. .... | Mar. 6, 1956  |
| 2,772,158 | Elliott .....       | Nov. 27, 1956 |
| 2,804,388 | Marron et al. ....  | Aug. 27, 1957 |
| 2,923,703 | Bruni et al. ....   | Feb. 2, 1960  |

##### FOREIGN PATENTS

|         |                     |              |
|---------|---------------------|--------------|
| 645,825 | Great Britain ..... | Nov. 8, 1950 |
| 402,737 | Great Britain ..... | Mar. 5, 1932 |

##### OTHER REFERENCES

Fischer, Colloidal Dispersions, copyright 1950, 2nd printing, June 1953, pub. by John Wiley & Sons, New York, pp. 91-94.

Boundy-Boyer: Styrene—Its Polymers, Copolymers, and Derivatives, Reinhold Pub. New York, copyright 1952, pp. 509 and 584.

UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,032,414

May 1, 1962

Raymond W. James et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 46, for "substane" read -- substance --;  
column 10, line 15, for "zince" read -- zinc --; line 18, for  
"d-diethyl" read -- p-diethyl --; column 16, line 10, for  
"8.6 X 10<sup>-10</sup>" read -- 8 X 10<sup>-10</sup> --.

Signed and sealed this 13th day of November 1962.

(SEAL)

Attest:

ERNEST W. SWIDER  
Attesting Officer

DAVID L. LADD  
Commissioner of Patents