

Nov. 3, 1959

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2,911,299

SYSTEM OF PHOTOGRAPHIC REPRODUCTION

Filed July 22, 1952

3 Sheets-Sheet 1

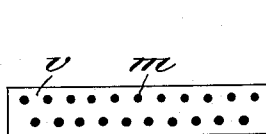


Fig. 1

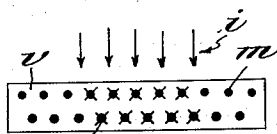


Fig. 2

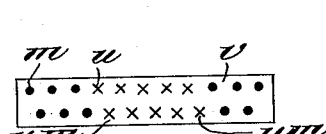


Fig. 3

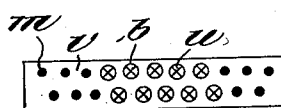


Fig. 4

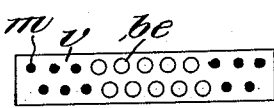


Fig. 5

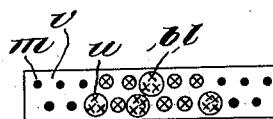


Fig. 6

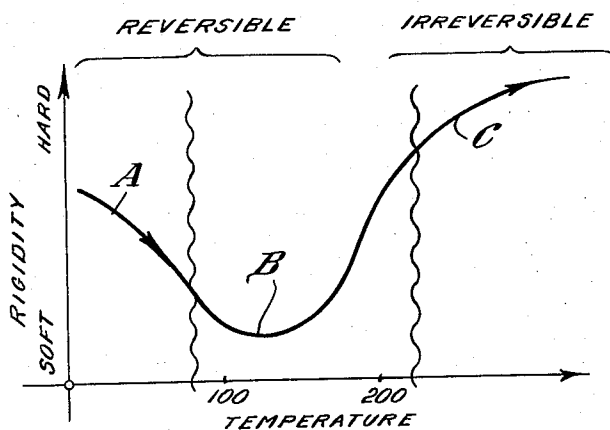


Fig. 7

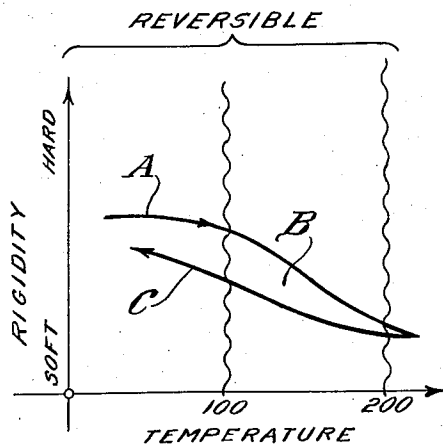


Fig. 8

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3 Sheets-Sheet 2

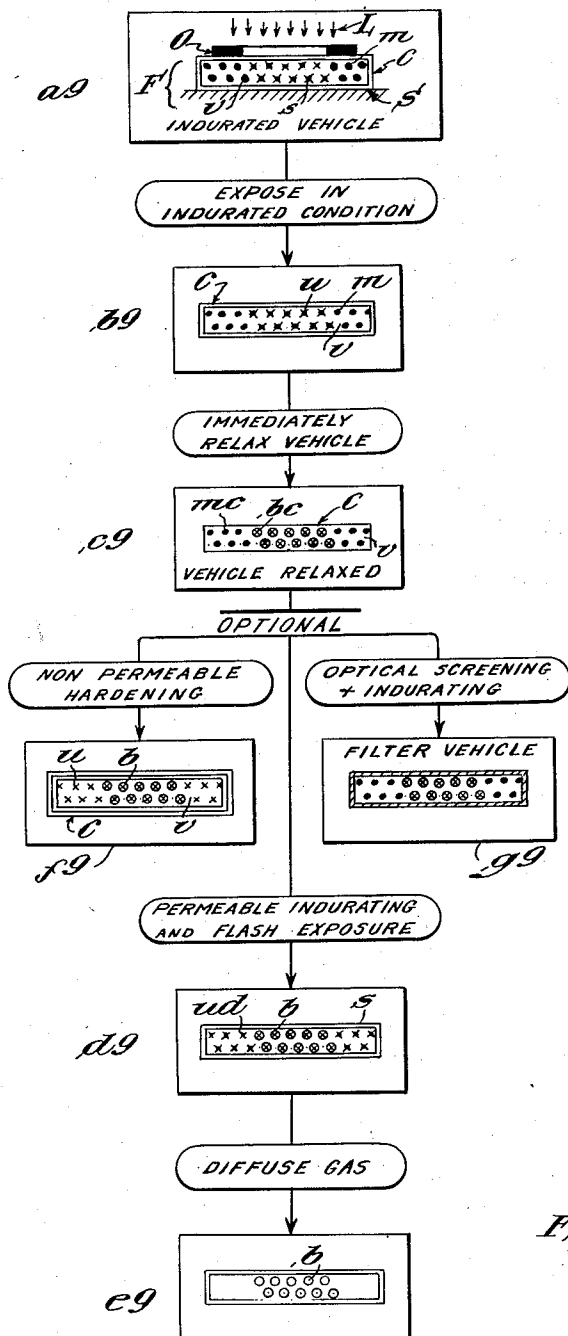


Fig. 9

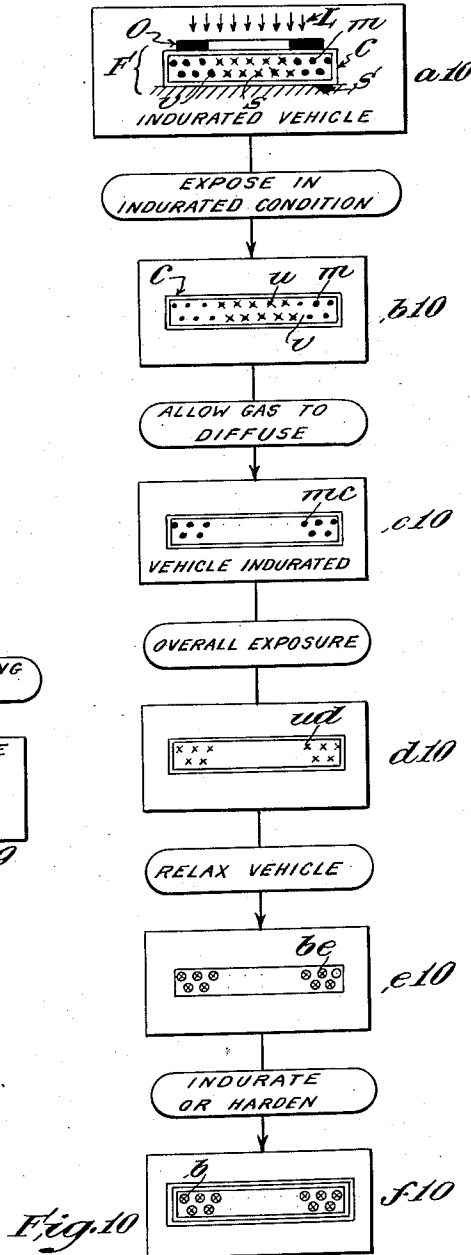


Fig. 10

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3 Sheets-Sheet 3

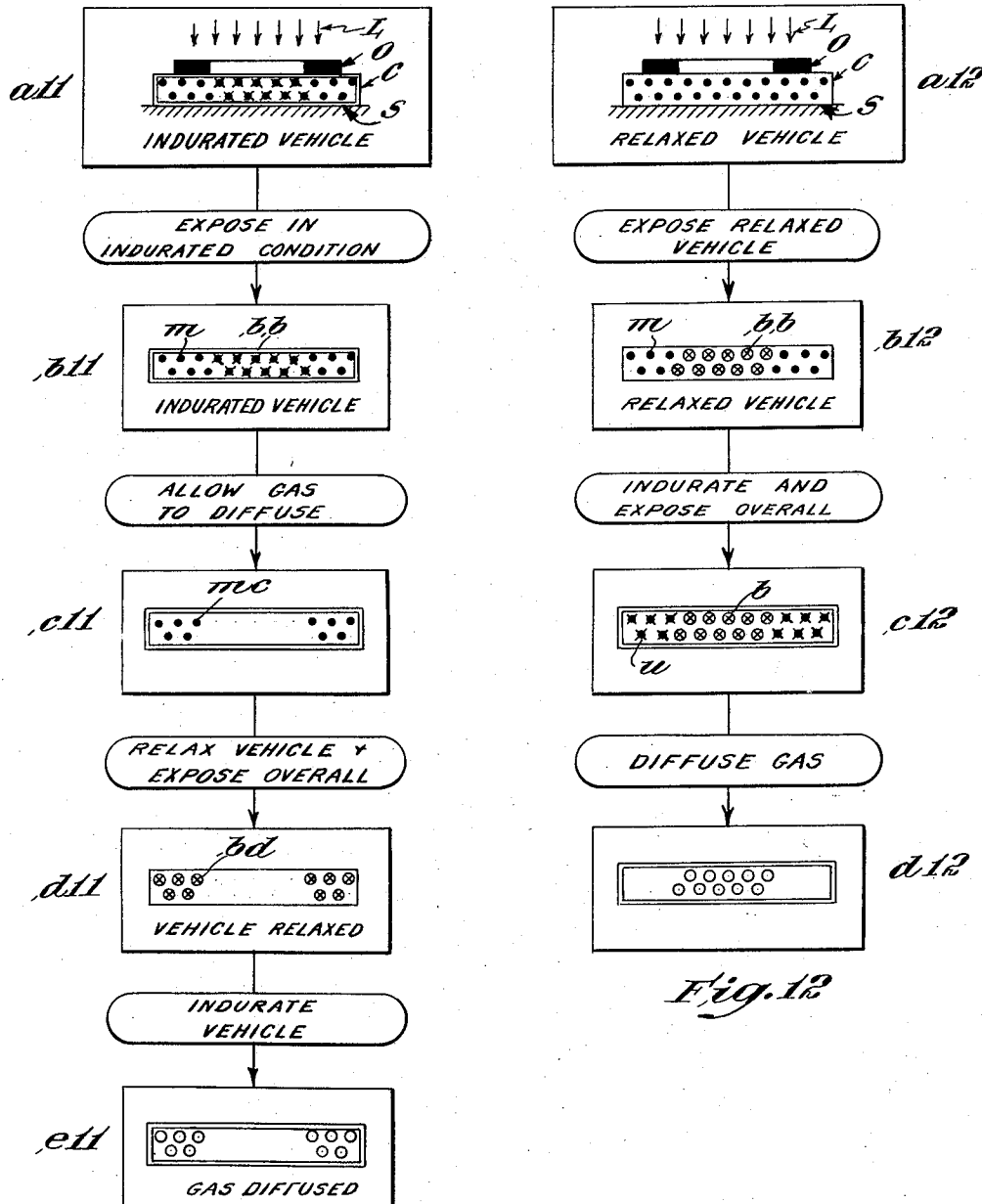


Fig. 11

Fig. 12

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SYSTEM OF PHOTOGRAPHIC REPRODUCTION

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Application July 22, 1952, Serial No. 300,282

1 Claim. (Cl. 96—49)

The present invention relates to a process of forming copies of records such as printed matter or microfilms by means of compounds which produce gas upon irradiation, and also to material wherein such copies can be formed, and to the copies themselves.

It is a principal object of the invention to provide photographic reproductions according to a technique which is extremely simple and inexpensive and yet fully satisfactory particularly for use in offices, libraries, drafting rooms and similar establishments where it is desirable to copy record material with a minimum of effort, with unskilled labor, and in minimum time.

Another object is to provide such a technique which employs material that is comparatively inexpensive, stands up well through reasonably rough routine handling, and produces exact and permanent copies.

Further objects are to provide a reproduction technique which is dry throughout and does not require chemical treatment or rinsing baths, and 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.

In accordance with the invention, an essentially stable photographic record is produced in a vehicle of adjustable rigidity containing a sensitizing substance capable of liberating gas upon exposure to radiation, in the form of gas sources or units that are essentially invisible upon generation and while the vehicle remains indurated but which are capable of expanding into visible bubbles within the relaxed vehicle, by exposing a layer of the vehicle in either indurated or relaxed condition to a radiation image thus forming therein a record in terms of gas units, by relaxing or indurating, respectively, the vehicle to bring it into the other condition with image selected units expanding into bubbles to form a final visible record, and by rendering ineffective the sensitizier which might remain within the vehicle in portions which are not occupied by the bubbles which form the final record, thus fixing the record against further exposure; in an important embodiment the fixed vehicle is in irreversibly hardened indurated condition.

In a practically important aspect of the invention, a layer of the vehicle is exposed in indurated condition to form therein a record in terms of gas units, the vehicle is then relaxed to form a record in terms of bubbles, and the sensitizier which after exposure remains within the vehicle is rendered ineffective and the copy fixed by uniformly exposing it and by diffusing the gas units thus formed from the indurated vehicle, or fixation is accomplished by permanently hardening the vehicle or by making the vehicle essentially opaque to gas liberating radiation.

In another aspect, a layer of the vehicle is exposed in indurated condition to form therein a record in terms of gas units, the gas is then permitted substantially to diffuse from the vehicle, an overall exposure is applied to generate gas sources from the remaining sensitizier, the vehicle is relaxed to expand the gas units resulting from the

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overall exposure to form a record in terms of bubbles, and a fixation step is applied.

In an additional aspect, a layer of the vehicle is exposed in indurated condition to form a record in terms of gas units, the gas is diffused from the vehicle, the vehicle is relaxed, and an essentially uniform exposure is applied to generate gas units from the remaining sensitizier which units expand into record defining bubbles; fixation follows.

In a further aspect, a layer of the vehicle is exposed in relaxed condition to form a record in terms of gas bubbles, the vehicle is then sufficiently indurated essentially to prohibit further bubble formation while permitting diffusion of gas, a substantially uniform overall exposure is applied to generate gas from the remaining sensitizier, and the remaining gas is permitted to diffuse.

Reproduction material according to the invention comprises a layer of vehicle material of adjustable rigidity and permeability incorporating an amount of sensitizing substance capable of generating sufficient gas to form a visible record in terms of gas bubbles upon exposure to radiation and expansion of the gas, the vehicle being characterized by a rigidity which is adjustable between optimal degrees, one of higher rigidity preventing substantial bubble formation but of sufficient permeability to permit gas unit formation and if desired gas diffusion from the vehicle, and the other of lower rigidity permitting gas bubble formation with permeability permitting escape of gas from the vehicle. In an important embodiment the vehicle is of the gelatin type, sufficiently indurated at ordinary temperatures to prohibit bubble formation, sufficiently relaxed at moderately elevated temperature to permit bubble formation, and becoming irreversibly hardened to a highly indurated condition upon heating to a further elevated temperature.

Final copies according to the invention comprise an indurated layer of plastic material of essentially uniform thickness which contains in substantially uniform distribution chemically unchanged photolytic decomposition products of a radiation sensitive substance, and essentially bubble shaped cavities distributed in a record forming pattern, the configuration of the individual bubbles as well as their distribution being fixed by the rigidity of the indurated vehicle. In an important embodiment the vehicle consists of irreversibly hardened gelatin.

Other objects, aspects and features will appear, in addition to those contained in the above statement of the nature and substance including some of the objects of the invention, from the herein presented outline of its theoretical basis and its practical possibilities together with the following description of several typical embodiments illustrating its novel characteristics. These refer to drawings in which:

Figs. 1 to 6 are diagrammatical cross sections through recording material according to the invention during various stages of the process according to the invention;

Figs. 7 and 8 are diagrams illustrating the rigidity adjustment according to the invention; and

Figs. 9 to 12 are diagrams illustrating four respective embodiments of the process according to the invention.

The following description presents first the general operational principles of the most important aspects of the invention with regard to the properties of vehicle and sensitizing substance, and then supplies specific examples of materials as well as of process sequences which incorporate these principles for various practical purposes.

The photographic reproduction system according to the invention is based on the possibility of determining a record pattern in terms of transmission, absorption, reflection and scattering of the incident light by the controlled formation of a structure of gas bubbles within a vehicle, coated on suitable sheet stock or self-supporting.

The primary photochemical reaction releases gas in a pattern determined by a radiation image, in proportion to the amount of radiant energy absorbed by a sensitizing substance.

The term "record" as herein used denotes any picture or indicia pattern in terms of effectively tangible characteristics of a body, such as texture or grain distribution. A record should be distinguished from a radiation "image" as defined by a beam that is modulated by an original record, in direct contact with the copying surface or related thereto through the intermediary of an image forming system. The term "original" is used for any object that modulates the radiation to which the sensitive substance is exposed; it can be a scene, an original picture or print, or a photographically or otherwise produced positive or negative copy. The term "radiation" as herein used includes electromagnetic radiation such as light within and on either side of the visible spectrum, as well as particle impingement.

The material which is used in the present system has two essential components in intimate cooperation, namely the vehicle and the sensitizing substance. A "vehicle" is the carrier or binder material for sensitizing substances and for the gas released therefrom upon photolysis, which gas occurs in the form of initial sources or units, and as record forming bubbles. A "sensitizing substance" or "sensitizer" for short, is radiation sensitive material incorporated in the vehicle which generates gas by decomposition upon irradiation.

The vehicle must have two properties in order to be usable for purposes of the invention, namely, permeability and adjustable rigidity.

The permeability has two important aspects, namely, the internal permeability or rate of diffusion of gas within the vehicle itself and the escape permeability, that is the rate at which gas can escape entirely from the vehicle.

The rate of diffusion of the gas within the vehicle itself (internal permeability) 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 the volume to pressure and temperature, respectively, after the release of what is herein referred to as "gas sources," from the irradiated sensitizing substance. 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. If these sources were trapped within the vehicle upon release by photolysis, they could not form the smallest units with the above characteristics of a true gas, which units might also be referred to as latent bubbles or bubble nuclei. These sources and units constitute an invisible latent record of the image defining radiation pattern which causes their release from the sensitizer within the vehicle. The gas contents of the units or latent bubbles varies to a degree which can be controlled by way of the internal permeability. The upper limit of internal permeability is determined by the spatial resolution required in the finished product, and hence by the size of the ultimate record forming bubbles. For example a microfilm print intended for projection use requires but a very small bubble. On the other hand reproduction for example of large size prints by contact exposure permits considerably larger bubbles. For a resolution of one thousand lines per inch, bubbles of approximately 2 microns are needed, and such a bubble would contain approximately 2×10^{-13} moles of gas. Accordingly, for applications requiring resolution of this fineness, the diffusion of the gas and hence the internal permeability of the vehicle has to be so adjusted that units containing substantially more than this amount of gas do not occur. Furthermore, the internal permeability has to be so regulated that the gas does not diffuse away from the exposed areas into unexposed areas where it might later cause general background fogging.

This property of the vehicle, providing for optimal internal diffusion of the gas, is illustrated in Fig. 1 where dots m represent molecules of the sensitizer which is dispersed in the vehicle v . In Fig. 2 crossed dots s represent sources of gas, generated by irradiation with a radiation image pattern i . At this stage the molecules released in photolysis cannot truly behave as a gas and, therefore, no bubble record can be formed if internal diffusion is so restricted that the partial volumes are small, containing only one or very few gas molecules.

The operative situation is represented in Fig. 3. Here the partial volumes are sufficiently large so that great numbers of the gas molecules can act together, behaving in units u as an ideal gas, and forming under high pressure the latent bubble agglomerates indicated as crosses which can expand to a maximum size determined by the rigidity of the vehicle, as will be discussed below. Fig. 3 also indicates how the record detail can be obscured or even expanded into the unexposed background, thus creating a fogged area, if diffusion is very great and marginal units um form beyond the actually exposed area.

While, as above discussed, the vehicle should be of sufficient internal permeability to allow the optimum diffusion of gas once formed therewithin, it should have a reasonably impervious surface so that gas is not completely lost from the emulsion during exposure, thereby reducing the efficiency and hence the sensitivity of the emulsion or the film. Efficiency is here defined as the ratio of the actual volume of gas confined in light scattering bubbles, to the amount released at standard conditions of pressure and temperature. This efficiency is affected by the above loss of gas and by the flow characteristics of the vehicle to be discussed below. Low efficiency means low sensitivity because it requires more energy to activate sufficient sensitive material to give a required contrast. The loss in sensitivity due to low efficiency cannot be compensated for by increased concentration of sensitizer because, if the concentration exceeds a certain rather critical value, then the gas units are initially too large and impair the resolution. A high efficiency therefore enhances sensitivity as well as detail resolution. The efficiency is also affected by the duration of those periods of the record forming technique during which the vehicle permits escape of gas.

The escape permeability of the vehicle furthermore affects the permanence of the final record which will be further discussed below. If after record formation the permeability of the vehicle is so changed that any further gas released by photolysis can escape quickly without forming bubbles, then the record is fixed against subsequent exposure. Thus, while it is in the interests of efficiency desirable to have a low rate of gas escape prior to record formation, it is desirable to have a high rate of gas escape thereafter. However, fixation is promoted by this gas escape only if the gas previously confined in the bubbles is no longer required to preserve the bubble structure. This, in turn, depends upon the rigidity characteristics of the vehicle which will now be discussed.

The rigidity characteristics of the vehicle have to conform to certain requirements during the principal steps of the present technique, namely, exposure, development, and fixation.

During exposure for the purpose of providing a latent record the vehicle, in addition to the above discussed internal permeability permitting formation of gas units, must have sufficient rigidity or resistance to flow to prevent the formation of expanded units or bubbles during exposure. Such bubbles would scatter light in the highlighted areas, thus cutting off further photolysis in these regions, causing insufficient exposure and reducing contrast. These considerations apply to exposure leading to formation of bubbles which constitute a final record, while they do not apply for purposes of preliminary,

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although pattern determining, exposure of a relaxed vehicle, as will be pointed out below with reference to a practical example of this type, illustrated in Fig. 11.

To convert or develop the record in terms of gas units or latent bubbles produced during exposure, into a visible record, the vehicle is relaxed in such fashion that the latent bubbles can expand to cross sections which will produce the maximum light-scattering effect consistent with the required resolution. Fig. 4 indicates this stage of bubble formation. The circles *b* which surround units *u* represent bubbles of desirable relative proportions. Fig. 5 indicates the record structure upon diffusion of gas from now empty bubbles *be*. These diagrams do not indicate possibilities of removing the remaining sensitizer *m*, which will be discussed below. In a practical and satisfactory embodiment, the average diameter for good resolution is about 2 microns, bubbles above 5 microns in diameter being undesirable.

In accordance with the present invention, the ratio of the cross section of the gas unit formed during exposure can be controlled for purposes of optimal utilization of the photosensitive material during exposure, and of increasing the overall efficiency of the whole photographic process. This ratio is therefore an amplification factor and will be so referred to herein.

Of equal importance to unit formation by internal diffusion is the increase in overall quantum efficiency that can be obtained by utilizing the gas amplification principle. The pressure under which the gas is released during exposure is a function of the concentration of the sensitive material, the primary quantum efficiency of decomposition of the photosensitive material upon irradiation, and the rigidity of the vehicle against which the gas must expand. In accordance with the invention these three variables are adjusted to limit the size during exposure to negligible light-scattering cross sections. We found that the gas amplification factor increases the overall quantum efficiency beyond that which can be obtained by coupling the decomposed material with a dye.

Fig. 6 indicates the undesirable condition where internal diffusion has been too rapid or relaxation gone too far so that large bubbles *bl* have formed which obscure the detail.

Development by relaxing the vehicle accomplishes the above discussed amplification by purely physical means. If the vehicle is a thermoplastic, the requisite conditions of plastic flow during development can be brought about by the amplification of heat by conduction, convection or radiation. The physical means for applying heat to obtain regulated relaxation and induration consistent with a large gas amplification factor can be quite simple, which is a primary advantage of the invention.

Fixation has the purpose of making the record stable and permanent in general use. The record must not disappear or be reduced in contrast or sharpness subsequent to development by losing its light scattering properties, it must be stable against fogging or accidental re-exposure, and it must be mechanically stable, that is sufficiently hard to withstand ordinary handling, including damage by scratching or softening under the heat of a projector lamp.

Preservation of the record proper can be accomplished by hardening the vehicle after the bubbles have been allowed their maximum expansion during development. This freezing of the bubble structure brings about fixation by sealing up each individual bubble to confine the gas therewithin, and by making the walls of each bubble sufficiently rigid so that even though the gas subsequently escapes, the wall remains, forming a light scattering cellular structure which is mechanically strong enough to maintain itself against ordinary use. It is this second aspect that is especially important since it preserves the record regardless of gas diffusion from the vehicles. This final hardening is especially beneficial because irreversible-

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ible and of a high degree, if the vehicle is of the gelatin type, as will be discussed more in detail below.

The vehicle can be stabilized against exposure and fogging by destroying detrimental sensitizer, by permanent hardening, and by optical screening.

The destruction of remaining sensitizing material which was not needed for formation of the final record, can be accomplished in several ways, three of which have proved to be especially important for the process according to the invention.

The first way is to make the material thermally unstable such as to prevent it from producing gas. This technique is applicable to the diazo sensitizer used in an important embodiment of the invention. Such material chemically decomposes at elevated temperatures, but in such a way that the yield of gas from thermal decomposition is much lower than it is for photodecomposition.

Another way of destroying the remaining sensitizer is the diffusion of the released gas such that, as rapidly as the gas is formed by photodecomposition, it escapes completely from the vehicle so that bubbles cannot form. Particularly effective is the combination of optical screening in the manner pointed out below and of slow diffusion of gas released thus destroying the remaining photosensitive material simply by exposure to a lower level of illumination than is required for initial exposure.

A third means of inactivating the remaining sensitizer is to eliminate a volatile component of the primary photochemical reaction. In a gelatinous vehicle for example, this can be accomplished by way of driving off the water that is required for the efficient release of gas by photodecomposition. At temperatures practical for relaxation development and fixation, most of the water is driven off. In the absence of water, the quantum efficiency of the photochemical reaction that remains possible is so much less than the quantum efficiency in the presence of water, that the sensitivity is greatly reduced.

Subsequent to the fixation process proper, the vehicle can be made too hard and resistant for bubbles to form readily under ordinary exposure conditions. Even though small amounts of gas are released by subsequent exposure it cannot expand into bubbles of significantly light-scattering cross section. This condition is essentially identical with that mentioned above as required for the rigid preservation of the cellular structure, and it goes hand in hand with the mechanical stability mentioned below which is desirable as a protection against scratching and other mechanical deformation in routine handling of the material.

Stabilization of the sensitizer is aided by changing the spectral transmission characteristics of the vehicle. The vehicle and sensitive material, before and during exposure, passes radiation of a critical wavelength required for the primary photochemical reaction. After exposure however, the spectral transmission characteristics of the vehicle can in many instances be so changed that it becomes opaque to light of the critical wavelength. This is in effect equivalent to wrapping up the unexposed parts of the film in black paper forever after. In the case of gelatinous vehicles carrying certain diazo compounds as sensitizers, for example, this can be accomplished concomitantly with the final hardening induration which in this instance somewhat tans the surface of the gelatin. This tanning and some coagulation within the emulsion renders the gelatin less transparent to the ultraviolet light in the general region of 3600 Å., so that the actinic spectral region mainly effective for image formation is filtered out.

Mechanical stability is in the main provided by the indurating and hardening procedures described above. A mechanical structure sufficiently rigid to preserve the bubbles which constitute the record, as well as to prevent the direct expansion of bubbles upon further exposure

is sufficiently hard to meet all the usual photographic needs.

In order to perform the above-outlined functions within the frame work of the invention, the materials employed therein are compounded and selected as follows.

The sensitizing substance must be capable of dispersion within the vehicle sufficiently fine for purposes of the required definition as further controlled by the above-discussed permeability and rigidity characteristics of the vehicle. 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 usable.

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, p-diethyl amino benzene diazonium chloride ZnCl_2 , 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-methyl-cyclohexylamino-benzene diazonium chloride, p-acetamino benzene diazonium chloride, 4-dimethylamino benzene diazonium chloride, 3-methyl 4-diethyl amino benzene diazonium chloride, 4-morpholinobenzene diazonium chloride, 4-piperidyl 2-5-diethoxy benzene diazonium chloride, 1-dimethyl amino naphthalene-4 diazonium chloride, 4-phenyl amino diazo benzene diazonium chloride.

Substances which liberate carbon oxides upon irradiation and which are useful for purposes of the invention are organic acids such as ferric ammonium citrate and oxalic acid.

For incorporating sensitizers in vehicles used for purposes of the invention, two techniques are feasible.

The sensitizing compound can be dissolved and in that state mixed with a solution of the plastic, and the mixture dried in the form of a film applied to a support. This technique is particularly applicable to gelatinous vehicles. Up to certain concentrations which depend on the particular gelatin, such vehicles contain the sensitizer most likely in molecular dispersion dissolved in the gelatin water. Above such concentrations the sensitizer is probably also dispersed in precipitated form, as will be discussed below with reference to the vehicle structure.

The sensitizing substance can also be incorporated in vehicles which are made from organosols which can be fused at temperatures below, although rather close to the decomposition temperature of the sensitizing substance, which condition must be taken into account in preparing such material.

The vehicle material plays a very important role within the framework of the present invention. It must lend itself easily to quick, positively controllable and reversible transformation from relaxed or amplifying condition into indurated condition, and vice versa, and in an important modification also to irreversible transformation into highly hardened condition. In either state, permeability is to be preserved, but in final irreversible induration or hardening the escape of gas can be excluded if desired.

In accordance with the invention, this transformation is accomplished by the purely physical expedients principally of temperature, and sometimes of moisture, or both. For most purposes dry heat is sufficient, with the ensuing practical advantages. The vehicle is for practical purposes of such a nature that it softens if the temperature is raised during the development process. As it softens, the gas units and bubbles are allowed to expand as above explained. After the bubbles have reached their

optimum diameter, another change in temperature leads again to induration, either of the reversible, or at choice of the hardening or final type. This cycle can be carried out for certain gelatin emulsions such as herein described. As the temperature is raised, gelatin of selected types softens somewhere between 100° and 200° F. allowing the bubbles to expand. As the temperature goes above 200° F., the gelatin tans on the surface somewhere between 200° and 250° F., and, in general, assumes a hard, rigid and irreversibly coagulated structure, which then provides the above discussed mechanical rigidity which freezes the bubble walls and preserves the structure even though the gas may subsequently escape. Vehicles of the Bakelite type are somewhat similar. They become plastic at an intermediate temperature of about 200° F., the approximate temperature required for expansion of the bubbles, and at a higher temperature of about 250° or 300° F., polymerize irreversibly.

Other vehicle characteristics can be utilized with slight modification of procedure. For example, a completely thermoplastic vehicle can be used which, when warmed to about 200° F. flows quite freely, thus providing the characteristics necessary for development by bubble amplification. Such a material need not have thermo-setting properties if it can be indurated by cooling it rather rapidly after development has taken place. Such reversibly controllable materials can be re-exposed and re-developed by proper sequences of heat and light application, but can be rendered stable against the application of heat alone or light alone as might be encountered in subsequent use. Still another type of vehicle material can be cooled rapidly enough after development to assume an irreversible structure or degree of hardness that requires the application of extremely high temperatures to plasticize it again, being in this respect somewhat analogous to the first mentioned type.

For any particular material, the optimum temperatures on either side of the transition points between relaxed and indurated conditions depend to some extent upon the technique of printing. The vehicle has to be chosen with regard to the relation between bubble gas pressure, rigidity, permeability, and to some extent also with regard to the record characteristics required, which may vary according to emphasis on fine grain, density, or other properties.

Figs. 7 and 8 illustrate the above-described temperature determined rigidity characteristics, which are a principal expedient within the process according to the invention.

Fig. 7 relates to vehicle material of the gelatin or bakelite type, which exhibits upon increase in temperature three distinct regions of induration. The low temperature range marked A represents an indurated yet permeable phase which is mainly employed during exposure of the areas of the final record. In range B the vehicle is relaxed permitting bubble expansion or development. In range C, the vehicle indurates permanently and to a higher degree. This cycle is reversible so far as ranges A and B are concerned but irreversible from range C. It will appear hereinbelow that the invention can be carried out within the reversible transformations between A and B, without reaching C, although use of the latter constitutes an important aspect of the invention.

In the case of gelatin vehicles, the function of range C is particularly assured through the tanning and hardening of the surface layer of gelatin, which acts somewhat as a barrier for the re-entrance or re-absorption of water. Such vehicles are as hard and stable mechanically as ordinary photographic emulsion.

Fig. 8 illustrates another cycle which can be carried out with thermoplastic vehicles which do not have a permanently indurated phase, but also with vehicles of the gelatin type if range C is not used.

Expedients other than heat can be used alone or in cooperation with a temperature cycle. Such an expedient is moisture, especially for gelatinous vehicles. Another

expedient is the above mentioned optical fixation by way of changing the light transmitting characteristic of the vehicle in range C. In the case of gelatin the tanning effect which accompanies the hardening induration can be utilized for this purpose.

The internal structure of the vehicle is as important a characteristic as the rigidity itself. The ideal structure is a porous one, in which each little pore forms a completely sealed cell within which gas units can form during exposure. These cells should have negligible light-scattering properties, and hence be very small in relation to the final bubble size. In the gelatin type vehicles, the small cells actually contain water, namely the water of emulsification of the gelatin. This water contains the sensitizer in solution, whereas precipitated sensitizer forms on the cell walls. It is within these small cells that the gas is released and collected during exposure. In other vehicle types the cells are formed by plastic walls and contain only such gas as is entrapped during the compounding of the vehicle.

The support can be of any suitable material, which will be transparent if the exposure takes place there-through or the reproduction is intended to be a diapositive. Glass, acetate film and similar substances are satisfactory, provided they withstand the operational temperatures required.

Opaque supports will generally be flexible such as paper or synthetic sheet material. These supports can be of any desirable color. Depending on the reflection characteristics of the backing or support, the diffusing bubble record will appear thereon lighter or darker; this must be taken into consideration in describing the photographic sign of the record as will be pointed out below.

Example 1

100 g. of high grade dry gelatin such as 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 g. citric acid C.P., and 10 g. of the sensitizing substance sold under the trade designation "Edwal Compound #8," which is a zinc salt of para diazo dimethyl-aniline. This is then diluted to make 2000 ml. This emulsion is coated by conventional means on glass plates or cellulose film of the types used for purposes of commercial photography, to a thickness of about 2 mils to 0.6 mil., rather less than more, depending on process control details and record requirements. This material, coated on a commercial cellulose film, is for example exposed to an original film in conventional contact or projection printing apparatus for copying microfilm, such as a blower cooled standard 35 mm. film projector modified for use as a contact printer with the film stage which consists of two spring loaded glass rectangles, holding the original film to be copied and the film to be exposed in a plane perpendicular to the optical axis.

The exposure time depends upon the output of the exposure lamp in the range of spectral sensitivity of the material (here within a band between about 3000 Å. to 4200 Å.), upon the density of the original, and upon the efficiency of the light gathering system used. Exposure times ranging from one second to several minutes have been successfully used for the above material.

The gas is then allowed to diffuse for about 30 minutes or less, depending on the thickness of the vehicle layer; 5 minutes is the average for thin films. The film is then relaxed by heating it for a few seconds to about 200° F., between two metal plates which are electrically heated and thermostatically controlled, or by infrared radiation. This is a heating within the reversible range discussed above with reference to Figs. 7 and 8. An overall exposure is then applied, of an intensity and duration which are about the same as required for the above exposure through the original.

If it is desired to harden the vehicle irreversibly, in region C of Fig. 7, a temperature of about 250° F. is ap-

plied, in the manner described above for the developing procedure within the reversible ranges A, B of Figs. 7 and 8.

Example II

5 50 g. gelatin, as above, are compounded with 1000 ml. water. To this are added 2.5 g. ferric chloride and 2 mg. oxalic acid. The emulsion is coated on a support, as above.

10 The salient practical features of the process technique according to the invention will now be described with reference to the above explained basic concepts. Exposure, rigidity control, and fixation will first be described with regard to general requirements and specific process examples will then be given.

15 The record forming exposure should be of fairly high intensity in view of the facts that most sensitizing substances at disposal for present purposes are only moderately sensitive, and that prolonged exposures are not only undesirable from the point of view of shop or office practice but might introduce temperature changes within the vehicle which cannot be easily controlled or prevented. It is possible to utilize an illumination source for heating the copying material, but the control of such heating complicates the printing setup. Short time high intensity exposure such as by way of arc lamps with efficient reflectors, placed fairly close to the printing material, was found to be quite satisfactory, permitting exposure times of a few seconds which order of magnitude can be easily managed by comparatively unskilled operators. This is important since the prescribed exposure time is fairly closely tied to the properties of original and copying material and should be rather carefully adhered to.

20 Conventional contact or projection printing apparatus can be used for purposes of the invention. In an installation for copying microfilm, a blower cooled standard 35 mm. film projector has been modified for use as a contact printer. The projection lens can be used to observe the films during exposure. The condenser system efficiently collects the projector lamp light to channel a maximum proportion thereof through the film to be exposed, and to permit the use of smaller light sources. For other purposes, exposures have been made directly by General Electric AH-6 mercury arc lights, by photo-flood lamps, and by projection lamps alone, in the film stage of microfilm readers.

25 The rate of gas diffusion from the exposed areas of a particular vehicle sets an upper limit on the length of exposure. Underexposure results in lack of record, or in thin records of inadequate contrast. Overexposure results in fogging at the edges of records due to sensitizer decomposition or bubble expansion beyond the record contours. Unless the sensitive material is purposely exposed in relaxed condition, care must be taken not to have the film so close to the light source as to permit heat to cause relaxation and hence development during exposure. Forced cooling can be used.

30 The emission spectrum of the source of radiation should be chosen with a view to the particular sensitivity of the sensitive substance. A preferred embodiment using "Edwal #8" in gelatin as above described, is sensitive to radiation within the wavelength band of 4200 Å. down to 3000 Å.; this permits the use of ordinary orange room light for handling.

35 Overall fixing and developing exposures such as will be described below are less critical. For most fixing purposes overexposure is harmless since complete exhaustion of sensitizing substance is desirable. Suitably diffused sources including daylight, are practical for this purpose. Overall reversal exposures are generally speaking similar to fixing exposures.

40 Rigidity control of the vehicle for purposes of development as well as fixation can be carried out in various ways as indicated above, mainly by application of heat or moisture or both.

Temperature control is the principal expedient for adjusting rigidity according to the invention. It can be effected by way of convection such as treatment in an oven or air stream, or by conduction such as by way of heat controlled plates or baths, or by radiation such as infrared rays. Combinations of such temperature control methods are possible and in use.

One practical method of heat treatment is to place the material after exposure in range A (Figs. 7 and 8) between two metal plates which are electrically heated and thermostatically controlled within the range of 180° F. to 235° F. This has been a thoroughly satisfactory development method for gelatin type vehicles. A few seconds suffice for development in range B, and an additional 5 to 20 seconds lead to range C and fixation through irreversible hardening of the vehicle.

For heating gelatin vehicles to range C, irradiation with infrared energy has also been found satisfactory. If properly controlled, this induces fixation through irreversible hardening of the vehicle and optical screening.

A method frequently used for developing gelatin vehicles is to combine temperature and moisture control by passing exposed material rapidly through an atmosphere or jet of low pressure steam. The warmth of the steam cloud or low pressure jet, somewhat below 212° F. and thus within the desired temperature range B, together with the moisture serve to develop out the latent record. It will be understood that these conveniently adjustable temperature and moisture controls are materially dependent upon initial and thereafter unchangeable selection of other factors, such as thickness and inherent porosity and plasticity properties of the vehicle material.

The relaxation time required for development is generally not very critical; between 2 and 5 seconds suffice in most instances for satisfactory development. For fixation there is no particular time limit.

Several methods for fixation of vehicle and record are practical and will now be described. As will become apparent from the practical examples, they can be used individually or combined, according to circumstances.

Application of heat for changing from relaxed condition in range B to indurated condition in range C or A (Figs. 7 and 8) is the principal fixation expedient. This change from relaxed developing to indurated nondeveloping condition involves mainly controlled and fairly rapid application of heat or quick cooling. The expedients used for changing from range A to B can be used such as hot plates, air blast devices and heat radiators, and temperature control is accomplished with conventional thermostats. In the case of gelatin vehicles, satisfactory fixation is accomplished by keeping the material between controlled temperature hot plates, beyond the required development time. A time of 5 to 20 seconds, depending on the temperature gradient, has been found to be adequate, leading to a great degree of permanence. Another technique is application of infrared light continued beyond the required development time.

Gas diffusion is another important fixation expedient. After development, the entire film surface can be exposed to light of intensity sufficient to cause photolysis. If the vehicle is then not placed again in development condition the released gas does not form bubbles but diffuses out of the film. Sufficient fixation exposure to destroy all photosensitive material not originally imaged exposed and developed has been achieved in times generally about the same as required for exposure of the record proper. After such exposure, the diffusion process requires from 2 minutes to 30 minutes, the time depending on the thickness of the vehicle layer.

Because of the availability of the diffusion method of fixation, it is not always necessary to introduce fixation as a definite step in the process. The developed material if put to routine use is in some cases necessarily exposed to sufficient light to complete photolysis in the previously unexposed areas. Thereafter, in ordinary storage, the re-

leased gas diffuses out and leaves the non-record areas clear and incapable of further change. It will however be understood that fixation according to the invention is in many cases an important and indispensable step.

Four different practical embodiments, some of them with optional variations will now be described by way of example. Since the underlying theoretical considerations and the procedural details which are selectively used in these examples are sufficiently described above, they will not now be repeated, unless specific circumstances call for one or the other detailed directions.

Due to the adaptability of the present system, it is very easy, by way of minor procedural changes, to make copies of the same as well as opposite photographic sign. As herein understood, the term "photographic sign" describes the general gradation relation of original and copy so that any reference herein to printing with the same sign means making a positive from a positive as well as a negative from a negative, and printing with opposite sign means the making of negatives from positives as well as of positives from negatives, the term positive and negative being used in a relative sense to express mutually complementary record patterns, independently of the character of the support which for this purpose is assumed to be transparent.

The adaptability of the present system is similarly advantageous with regard to the fixation procedure which can be easily modified for any practical purpose.

In Figs. 9 to 12, only the coatings C are mainly shown, for the sake of simplicity. The various phases undergone by the sensitizer are indicated in the same manner as in Figs. 1 to 6. The three vehicle conditions are indicated by single, double and triple contours, corresponding to temperature ranges A, B and C respectively.

Fig. 9 shows at a9 an original O directly superimposed upon a film F which consists of a coating C and a support S. The coating C comprises a vehicle *v* and a sensitizing substance indicated by dots *m*. The original O can for example be a microfilm and the two elements O and F can be exposed in the above-mentioned modified projector. Assuming that the coating is of the type described above in material Example I, the vehicle is at room temperature and hence in indurated condition corresponding to range A of Fig. 7. Upon exposure the original O impresses its record upon the beam L of collimated light, establishing a radiation image in terms of sources *s*. As indicated at b9, this exposure produces a record pattern composed of units *u*.

At c9, the vehicle is then relaxed as above described with reference to Fig. 7, by raising the temperature into range B. This induces expansion of the gas units *u* into gas bubbles *b*. The coating C now contains a record, corresponding to the original O, in terms of visible bubbles containing gas, and unexposed sensitizer *mc*. In order to fixate the record, various techniques can be employed in accordance with the invention, as discussed above. Three optional fixing procedures will now be explained.

As indicated at d9, the coating C can be brought into indurated condition by cooling it to region A which will inhibit expansion of the gas units *u*. A uniform exposure is applied and the gas developed during such exposure allowed to diffuse through the vehicle which, it will be remembered, is still permeable. The record defining bubbles *b* solely remain as shown at e9 of Fig. 9.

An alternative uses the possibility of hardening the vehicle in temperature region C, as indicated at f9 of Fig. 9. This arrests with safety any further expansion and it is in this case unnecessary to make certain whether or not an overall fixing exposure is applied and the gas permitted to diffuse.

A further alternative is shown at g9. In this instance the vehicle is rendered opaque for actinic light as indicated by cross hatching of the diagrammatical showing of layer C. As mentioned above, this technique of impart-

ing an optical filter action to the vehicle can be connected with the tanning in accordance with *f9* in which case fixation is even more safe, although it will be understood that either procedure *f* or *g* is sufficient, and that the respective steps can be separately applied by means which are expedient in any particular environment.

This modification results in a record of opposite photographic sign from that of the original.

As indicated in Fig. 10, the first two steps *a10* and *b10* are in this instance identical with steps *a9* and *b9* of Fig. 9. However, whereas according to Fig. 9 the vehicle is relaxed immediately after exposure in indurated condition, the gas is here given sufficient time to diffuse from the vehicle, as indicated at *c10*. A negative record in terms of sensitizing substance *mc* remains. At *d10* this is now given an overall exposure that converts the sensitizer molecules into gas units *ud*. The vehicle is thereupon relaxed, permitting the gas units to expand and form bubbles *be* as shown at *e10*. It will be noted that in this instance fixation is unnecessary so far as remaining sensitizer is concerned, but for mechanical reasons another induration can be applied as indicated at *f10*.

This technique produces a final record of the same sign as the original.

In the example according to Fig. 11, the first two steps are similar to *a9* and *b9* of Fig. 9, namely exposure and gas unit formation at approximate room temperature. The step *c11* is similar to step *c10*, namely the diffusion of the exposed portions, resulting in a negative record in terms of sensitizer molecules *mc*. The vehicle is thereupon relaxed and an overall exposure applied which results in a negative record in terms of bubbles shown at *bd*. The vehicle is then indurated or hardened in temperature region A or C, which results in the permanent record indicated at *e11*. It will be noted that this is the technique according to Example I.

The record *e11* is of the same photographic sign as the original.

As indicated at *a12* of Fig. 12, the vehicle is in this instance in relaxed condition during exposure. As indicated at *b12*, the irradiated sensitizer molecules immediately expand to form bubbles *bb*, whereas in the unexposed portions the sensitizer *m* is not affected. As indicated at *c12*, an overall exposure is then applied after the vehicle has been indurated. This preserves the record in terms of gas bubbles whereas the remainder consists of units. This record can then be fixed in any one of the ways described above with reference to Fig. 9. Fig. 12 indicates a preferred embodiment according to which the gas is permitted to diffuse from condition

c12, which provides an indurated vehicle record in terms of empty gas bubbles *bf*.

The record according to this modification is of opposite sign to the original.

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 claim.

We claim:

- 10 A method for producing essentially stable photographic records in terms of substantially purely textural changes of a vehicle whose rigidity varies reversibly within a given temperature range and which contains dispersed therein a photolytic compound capable of liberating gas upon irradiation which gas does not effect
- 15 said textural changes at a low temperature within said range but effects such changes at a vehicle relaxing temperature that is comparatively high within said range, comprising the steps of exposing said vehicle to record
- 20 defining irradiation in comparatively rigid condition at a temperature that is comparatively low within said range, diffusing said gas as liberated from the unchanged vehicle at said low temperature, and subjecting said vehicle
- 25 to said high relaxing temperature with application of essentially uniform irradiation, whereby gas is liberated from the previously less irradiated vehicle portions effecting development of said record defining textural changes, the photolytic compound is essentially eliminated, and
- 30 the record essentially fixed.

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