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PHOTOGRAPHIC PRODUCT COMPRISING A LIGHT-SENSITIVE DIAZONIUM COMPOUND, A COUPLER AND A RUPTURABLE CONTAINING MEANS HOLDING AMMONIA UNDER PRESSURE

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FIG. 1

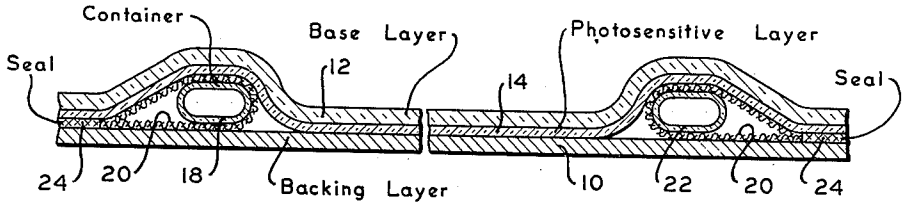
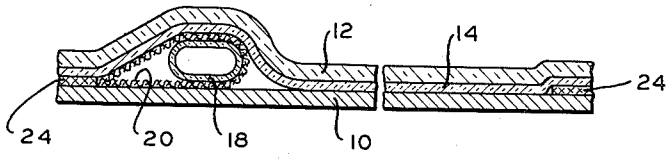


FIG. 2



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PHOTOGRAPHIC PRODUCT COMPRISING A LIGHT-SENSITIVE DIAZONIUM COMPOUND, A COUPLER AND A RUPTURABLE CONTAINING MEANS HOLDING AMMONIA UNDER PRESSURE

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8 Claims. (Cl. 95—8)

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This invention relates to photography, and more particularly to novel composite photographic film units.

One of the objects of the invention is to provide a novel composite photographic film unit comprising a photosensitive layer, another layer and gas-containing means mounted between said layers and adapted, on the application of compressive force thereto, to release the gas contained therein for spreading between said layers.

Another object of the invention is to provide a composite photographic film unit comprising a layer of photosensitive material, which includes a diazonium compound, and a substance, carried by a container, capable of causing an image-forming reaction to take place in portions of said diazonium photosensitive material which are unexposed to actinic light.

Still another object is to provide a novel, composite photographic film unit comprising at least a photosensitive layer having therein a diazonium compound, another layer, and fluid-containing means of a frangible material mounted in operative relationship with respect to said layers and adapted to be fractured, on the application of compressive force thereto, to release said fluid for spreading in contact with said photosensitive layer.

A further object is to provide a novel, composite film unit comprising at least a base layer carrying thereon a layer of photosensitive material including a diazonium compound, another layer, a frangible container for a fluid composition mounted between said layers, a seal for the adjacent edge portions of said base layer and said other layer, said seal and said layers being substantially impervious to the fluid in said container, and a substance contained within the sealed portion of said film unit capable of absorbing or combining with said fluid.

A further object is to provide a novel, composite film unit comprising at least a base layer, carrying thereon a layer of photo-sensitive material including a diazonium compound, another layer, a container for a fluid composition mounted between said layers, a second container having therein an absorbent for said fluid or a substance capable of combining with said fluid, and a seal for the adjacent edge portions of said base layer and said other layer, said seal and said layers being impervious to the fluid in said container.

A still further object of the invention is to provide a composite photographic film unit comprising a photosensitive layer, another layer, and containing means for a gaseous substance mounted between said layers and adapted, upon the application of compressive force thereto, to release said gaseous substance between said layers, said substance being capable of reacting with portions of said photosensitive layer to cause the production of a positive image in said film unit.

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Still another object of the present invention is to provide a novel, composite film unit comprising at least a base layer carrying thereon a layer of photosensitive material including a diazonium compound, another layer, a frangible container having therein ammonia under pressure, a second container having therein an absorbent for said ammonia or a substance capable of combining with said ammonia, and a seal for the adjacent edge portions of said base layer and said other layer, said seal and said layers being substantially impervious to the ammonia in said container.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

For a fuller understanding of the invention, reference should be had to the following detailed description taken in connection with the accompanying drawing wherein:

Figure 1 is an exaggerated, sectional view of one form of the composite film comprehended by the present invention; and

Fig. 2 is an exaggerated, sectional view of another form of the composite film comprehended by the present invention.

This invention relates generally to the use of a composite, photographic film unit comprising a photosensitive material which is capable of producing a positive image upon being processed after exposure to actinic light. The preferred embodiment of the invention contemplates the use of a photosensitive layer incorporating a diazonium compound. The film unit also contains within its confines all the materials necessary to create, by means of the selective color-forming ability of the diazonium compounds, a fixed positive image of the subject image to which said film unit is exposed.

In one modification of the invention, the photosensitive layer comprises a diazonium compound having incorporated therewith a coupler capable of coupling with unexposed portions of said diazonium compound and an acid which normally prevents this coupling. The film unit contains, in releasable form, an alkali capable of neutralizing said acid to permit said coupling reaction to take place. This alkali is preferably carried by a suitable container and may be in the form of

a gas, a liquid, or a liquid solution; or it may be in solid form and the film unit may contain a solvent therefor in releasable form.

Another modification of the invention contemplates the use of the same general type of photosensitive material which does not contain a coupler or an acid. In this case, the coupler and an alkali are preferably carried in solution in a container embodied within the confines of the film unit and whose contents may be released by the application of mechanical stress to the film unit.

A preferred modification of the invention contemplates the use of a composite photographic film unit of the type shown in Fig. 1. In this figure, the film unit comprises a base layer **12**, which may be a suitable cellulosic film base, such as cellulose acetate, cellulose nitrate, or cellulose acetate butyrate. This base layer has coated thereon a photosensitive layer **14**, which, in a preferred embodiment, comprises a diazonium compound such as that of N-ethyl-N-(4-amino-3-methyl-phenyl)-glycineamide, having incorporated therewith a suitable coupler such as B-naphthol and an acid such as hydrochloric acid, to prevent coupling. Numerous other examples of suitable ammonia-developable diazonium photosensitive layers are given in United States Patents 1,870,930, 2,150,565, 1,936,957, 1,989,065, 2,209,087, 2,228,562 and 2,286,656. Discussions of the theoretical considerations involved in the various diazonium photographic processes are found in the following publications: Clerc: "Photography, Theory and Practice" (second edition, 1944 reprint), page 444; Neblette: "Photography Principles and Practice" (fourth edition, fourth printing 1944), pages 226–7, pages 703–4; Friedman: "History of Color Photography" (1944), pages 487–493; D. J. Brown: "The Basis and Practice of the Diazo-Type Process," "Chemistry and Industry," April 15, 1944, pages 146–148. There is also provided another layer **10**, which acts as a backing layer and is preferably formed of a material which is substantially impervious to a gas and may be a plastic sheet or paper having a plastic coating. The layer **10** is of such impermeability as to permit the fluid used for producing a visible image to escape from the film unit so slowly as not to interfere with the photographic reactions.

Layer **10** can be either transparent or opaque depending upon the intended use of the composite film unit. At one end of the film unit, there is provided a container **18** adapted to have therein a fluid composition which, in a preferred embodiment, may be gaseous ammonia under pressure. The container is preferably gas-tight and a preferred embodiment contemplates the use of a gas therein. This container may be relatively flat and the gas may be under pressure therein, so as to permit the storage in a small space of a sufficient volume of gas to carry out the desired reactions . The container may be suitably scored or etched in places so that the container may be fractured by the application of a mechanical stress thereto, and so that the container will break into relatively large pieces.

Surrounding container **18** there is provided a filter **20** which may be formed of filter paper or cloth, such as a gauze. The purpose of this filter is to retain the fragments of the container after the fracture thereof and also to provide a convenient means for securing the container to the film unit. As shown in Fig. 1 only at both ends, there is provided a seal **24** which completely surrounds the whole film unit and is adapted to form the film unit into a gas-tight unitary structure so that gas released therein cannot escape therefrom. The film unit is gas tight in the sense that the gas released therein is kept from escaping for a sufficient length of time to permit the complete reaction of the gas with the reactive material in the photosensitive layer. The film unit is also preferably so impervious to the gas that no substantial quantity of the gas will escape therefrom and the gas can be removed by absorption by or chemical reaction with a material contained within the film unit.

A second container **22** is additionally provided with a second filter covering **20** and positioned at the opposite end of the film unit from the first container **18**. This container also preferably comprises a glass shell having therein a substance adapted to react with the gas in container **18**, either by absorption or chemical combination therewith. The container **22** may be scored or etched to permit easy fracture thereof in the same manner as discussed in connection with container **18**.

In the use of the invention shown in Fig. 1, the photosensitive layer **14** is exposed to actinic light such as in a camera or in a duplicating apparatus. This exposure is preferably through the base layer **12**. Wherever the light hits the diazonium compound, it destroys the ability thereof to couple with the coupler also contained in the photosensitive layer. Where the light has not reached the photosensitive diazonium compound, this substance can couple with the coupler whenever the acid is neutralized. In order to produce a visible image in the photosensitive layer, it is necessary only to fracture the container **18** to release the ammonia gas carried thereby. Due to the fact that the ammonia is under considerable pressure, it escapes from the container **18** and completely fills the composite film unit, and neutralizes the acid contained in the photosensitive layer. When this acid is neutralized, the unexposed photosensitive material couples with the coupler and a positive colored image is obtained in the photosensitive layer. Due to the fact that the outer layers of the composite photographic film unit are substantially gas-impervious, and also due to the fact that these layers are sealed together by a gas-tight seal, the ammonia released within the film unit cannot escape.

It is desired, however, to remove any ammonia remaining after neutralization of the acid, since, in many cases, it may be desirable to separate the base layer **12** and photosensitive layer **14** from the backing layer **10**. In order to accomplish this function, it is contemplated by the present invention to include in the container **22** a substance which is capable of removing ammonia vapor either by absorption or by chemical reaction. As a preferred example, the container **22** may have therein a substance such as charcoal or felt, saturated with water, which will absorb any excess ammonia vapor. Since it is desired that this absorption be accomplished after the ammonia has completely reacted with all the acid in the photosensitive layer **14**, so as not to hinder the neutralization of such acid, it is preferred that these absorbing materials be kept out of contact with the ammonia until such time as the neutralization reaction has been completed. The container **22** may then be fractured after a predetermined period of time to allow the ammonia to contact the absorbent and to be ab-

sorbed thereby. In some cases, it is desirable to use a strongly reactive material, such as sodium bisulfate, for reacting with ammonia to create therewith solid compounds. In this case, the ammonia shoud be kept out of contact with the sodium bisulfate until such time as the acid neutralization reaction is complete. Then the container 22 is fractured and the ammonia gas allowed to enter. In connection with the use of sodium bisulfate, in view of the reactive characteristics thereof, the container is preferably modified so as to permit the entrance of ammonia gas without permitting the egress of the sodium bisulfate. Such a modification may be readily accomplished by providing a small neck for the container 22, which may be broken off so as to permit gas to enter, while preventing any escape of the sodium bisulfate. Although such a construction is not shown, its design should be apparent to one skilled in the art.

It is also contemplated to utilize materials for neutralizing the rather offensive characteristics of ammonia gas other than those listed above. Some of these materials react rather slowly with ammonia and therefore need not be placed in any special gas-impervious containers. Examples of such materials are certain solid organic acids such as tartaric, citric or oxalic acid. When these solid organic acids are utilized, they may be deposited on the inner surface of the backing layer or can be incorporated in a porous substance, such as a piece of felt, positioned near one end of the film unit. It is also possible, of course, to have these organic acids in solution and carried by a container such as container 22, so that they may be released within the confines of the film unit to contact the ammonia gas and absorb this gas. In view of the absorptive qualities of water and the fact that the presence of an acidic water solution would interfere with the coupling operation when these acids are carried in solution, it is preferred that they be released after the neutralization of the acid in the photosensitive layer has been accomplished and after the positive image has become fully visible.

It is also contemplated by the present invention to utilize, as materials for causing the production of a visible image in a photosensitive layer, substances which are in a liquid solution rather than in a gaseous form. A preferred embodiment for this particular feature of the invention is shown in Fig. 2. In this figure, like numbers correspond to like elements of Fig. 1, and as shown, there are provided a base layer 12 and a photosensitive layer 14. The photosensitive layer preferably comprises a diazonium compound of the type discussed in connection with Fig. 1 and which has incorporated therein a coupler and an acid to prevent the coupling reaction. The backing layer 10 may be transparent or opaque and is preferably sufficiently impermeable to a liquid composition to prevent escape of liquid composition therethrough. A container 18 like container 18 of Fig. 1 is also provided, and a filter 20 is utilized for retaining the pieces of container after the container has been broken. Container 18 preferably carries a liquid composition comprising an aqueous solution of an alkali plus a viscous film-forming material. Such a liquid composition may comprise a solution of water, sodium carboxymethyl cellulose and an alkali such as sodium carbonate or sodium hydroxide. The liquid composition also preferably includes a mild reducing agent.

The nature and use of such mild reducing agents are discussed in the previously mentioned Brown article and in United States Patent 1,841,653.

In the use of the photographic film unit of the type shown in Fig. 2, the photosensitive layer 14 is exposed to actinic light, preferably through the base layer 12. The container 18 is then fractured such as by passing the film unit through a pair of pressure rollers. This releases the liquid composition which is spread in a uniform film between the photosensitive layer 14 and the backing layer 10. By the use of a viscous liquid which is spread in the form of a film, it is possible to obtain quite accurate control of the amount of alkali made available to each individual portion of the photosensitive material, and it is possible to so adjust the quantity of alkali contained in the liquid composition and the thickness of the film spread in contact with the photosensitive layer that the alkali will just neutralize the acid contained in the photosensitive layer and there will not remain a surplus of alkali which might tend to discolor the highlights of the final image. The presence of the reducing material also aids in the prevention of this discoloration, which is ordinarily due to aerial oxidation of the excess coupler remaining in the photosensitive layer. With such a modification of the invention, the formation of a film acts to dry up, to a certain extent, the water carrying this film-forming material in solution and therefore rapidly dries the finished positive print, so that the print can be utilized very shortly after processing. In a preferred form of the invention, the formed film is separated from the photosensitive layer 14, along with the backing layer 10, and is discarded. This leaves the photosensitive layer perfectly dry with a positive, stable image therein.

Although the invention of Fig. 2 has been described in connection with the use of a container made of a frangible material, it is contemplated that this invention may be equally used with a rupturable container of the type described in connection with my application Serial No. 578,379, filed February 17, 1945, for Photographic Products (now abandoned and replaced by application Serial No. 64,870, filed December 11, 1948, which latter application matured into Patent No. 2,543,181 on February 27, 1951). In some instances such a container is preferred to the glass container, since it is more susceptible to mass production.

In general, such a container comprises a sheet of metal foil coated with a resin, such as polyvinyl butyral, which is inert in alkalis. This sheet is folded over upon itself, filled with liquid composition and heat sealed on the three edges, the seals at the ends being made stronger than the seal at the edge opposite from the fold. Thus, when the container is subjected to stress, the liquid is released therefrom in a unidirectional manner.

It is also contemplated by the present invention to include in the container 18 of Fig. 2 the coupler adapted to couple with the unexposed portions of the photosensitive material. In this case, the photosensitive material does not ordinarily contain an acid, since it is not necessary to prevent any coupling before the coupler is brought into contact with the unexposed photosensitive material.

It is also contemplated by the present invention to have in the container 18 only a sol-

vent for the other materials utilized in the processing of the film unit. For instance, the backing layer 10 may have coated on its surface, in solid form, a mixture of sodium carboxymethyl cellulose, an alkali and a mild reducing agent. In this case, the container 18 has therein only water, which, when released, is spread between the photosensitive layer and the backing layer. The water dissolves the coating materials and transports them in the form of a solution to the photosensitive material where the reactions take place in the same manner as discussed above.

Since the present invention involves, in all of its various modifications, the provision of a composite photographic film unit containing in releasable form all of the materials required in the production of a final positive image in said film unit, this composite film unit may be utilized to advantage in that it can be developed without recourse to a darkroom or other special treatment. The film may be processed in the camera utilized for exposing the film, and when removed from the camera there is obtained a final, stable, positive print. Such a construction has the inherent advantage that the user of the composite film unit of the present invention need only purchase the camera and does not have to provide any special apparatus for treating the film. It is only necessary that the camera be provided with some means for applying mechanical stress to the film to cause the formation of a positive image.

It should also be understood that, although the invention has been described in terms of individual film units, it may be practiced with roll films wherein a plurality of images are produced and the roll film may be treated so as to produce each image separately or all images simultaneously.

Since certain changes may be made in the above product, and different embodiments of the invention could be made without departing from the scope of the invention, it is intended that all matter contained in the above description or shown in the accompanying drawing shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A photographic product containing material, including a photographic reagent, for producing a development of a visible image in said product, said reagent being present in an amount sufficient to effect said development, said product comprising a fluid-confining layer including at least a photosensitive portion comprising a light-sensitive diazonium compound and a coupler therefor, said photosensitive portion being capable of having a developable image formed therein upon photoexposure, another fluid-confining layer, and a rupturable containing means holding ammonia under pressure, said ammonia being in an amount sufficient for developing said image in said photosensitive portion, said ammonia, upon permeation of said photosensitive portion, being effective to develop said image, said layers being superposed with said containing means therebetween, portions of said layers being sealed together to provide an envelope including therewithin said containing means and said photosensitive portion so that rupture of said containing means permits permeation of said photosensitive portion by said ammonia, said envelope being sufficiently gas-tight to confine said ammonia within said envelope at least until said development has been effected.

2. The product of claim 1 wherein said product additionally includes a material capable of absorbing ammonia.

3. The product of claim 1 wherein said product additionally includes a material capable of reacting with ammonia to form therewith odorless compounds.

4. The product of claim 1 wherein said second layer includes a material capable of slowly neutralizing ammonia.

5. The product of claim 1 wherein said product includes a vapor-impervious container including an absorbent for ammonia.

6. The product of claim 1 wherein said product includes a vapor-impervious frangible container including sodium bisulfate.

7. The product of claim 1 wherein said product includes a vapor-impervious frangible container including a porous material impregnated with water.

8. The product of claim 1 wherein the second layer includes a solid organic acid.

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