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G. P. HAM

2,196,901

PHOTOGRAPHIC DEVELOPER

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FIG. 1.

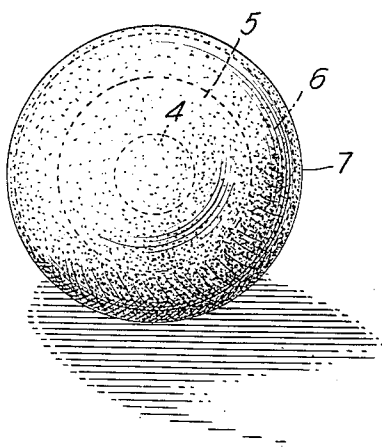


FIG. 2.

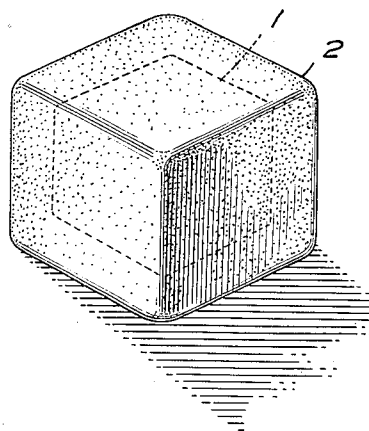


FIG. 3.

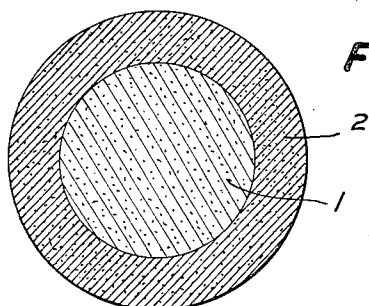


FIG. 5.

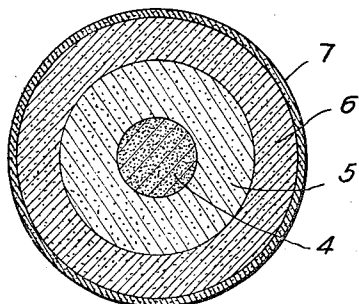
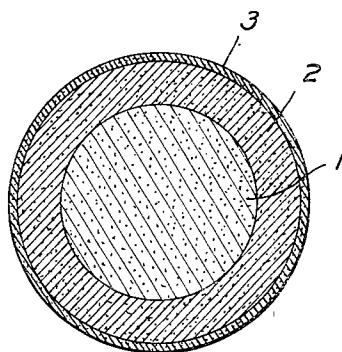


FIG. 4.



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PHOTOGRAPHIC DEVELOPER

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11 Claims. (Cl. 95—38)

This invention relates to a product for use in preparing photographic developing baths. It particularly relates to a molded block which contains the necessary chemical components for a photographic developer arranged in such a manner that when placed in water they will dissolve in a pre-determined order.

Photographic developing baths in general use are aqueous solutions containing various developing agents, various sulfites, various alkaline carbonates or hydroxides, and in many cases, restrainers such as the alkaline earth metal bromides. Other chemical compounds are often added to achieve some particular function, such as to obtain added preservation against aerial oxidation, or materials such as sodium sulfate to minimize the softening of the gelatin emulsions.

In the preparation of these photographic developing solutions it is necessary that the various chemicals be dissolved in a definite order to obtain satisfactory results. For example, a photographic developer containing an alkali, a preservative such as sodium sulfite, and a developing agent such as Metol and hydroquinone, require that the developing agents and at least part of the sodium sulfite be dissolved prior to the dissolution of the alkali. If a portion of the alkali is dissolved prior to the dissolution of the sodium sulfite and developing agent oxidizes and the developer is destroyed.

In the past, developers have been sold either in the form of prepared solutions or in solid form. The solutions are open to numerous objections. The keeping qualities are somewhat inferior and many developers of high energy are not suitable for marketing in solution form at all. When the developer components are used in solid form it has been necessary either to dissolve up the chemicals separately or where individual packages, cartons or tubes have been supplied, the developer has been divided into two components, one of these containing the developing agents proper and a part of the sulfite and the other, the remainder of the chemicals. In each of these cases, care had to be taken to dissolve the components in the right order and to be sure that each component was completely dissolved before the introduction of the following one.

In the past these various compounds have been supplied in individual packages, cartons, bottles, tubes, concentrated solutions, etc., and each compound was dissolved separately in the bath in order as directed by the formula. This meth-

od of supplying the chemicals is not particularly objectionable to the large commercial users such as photoengravers, large X-ray laboratories, and others who have the necessary facilities for weighing, measuring, and preparing the finished solutions. However, it is not satisfactory for the amateur photographic developer or for X-ray development in small laboratories or by dentists and physicians, because usually such persons do not have the proper facilities, time or inclination for weighing, measuring, and dissolving the various ingredients. As a result unsatisfactory developing solutions are frequently prepared and hence faulty photographic results are obtained.

According to the present invention I have discovered a method whereby all the various components of a photographic developing bath are combined in a single solid composition and in such a manner that the various components are selectively dissolved in a pre-determined order when placed in water without requiring any skill on the part of the operator.

The solid composition according to the present invention may be in the form of a molded cube or brick which is a convenient form for conserving space in packing and shipping. In another embodiment of the invention the solid composition may be molded in the form of a sphere. In both cases the components should be arranged in concentric layers which will permit substantially complete solution of one layer before the next layer dissolves. According to the present invention the ingredients of solid composition may be arranged individually in concentric layers or two or more of the ingredients may be combined in a mixture and the mixtures then arranged according to any desired order in layers.

It is an advantage of the present invention that a complete photographic developer is made available in a solid form requiring only solution in the water and a method is provided by which photographic developing baths can be prepared without any danger of producing oxidized solutions and without the necessity for weighing and measuring the various components. It is also an advantage of the present invention that photographic developing compositions which do not keep in solution are provided in a form that will permit readily the preparation of any desired quantity of a fresh solution. This feature permits substantial savings over prior methods. For example, in three color separation negative development in photo-lithographic or photo-engraving work, the developer solutions must be

used fresh in order to insure proper contrast of the negatives. This requires the preparation of a large number of developing solutions during the working day and thus the present invention will result in a considerable saving in both time and expense.

Another field in which the present invention can be used to good effect is with combined developers and fixers of the so-called "Monobath" type which permit development and fixation by means of the same solution and are employed in cases where it is desired to develop to a uniform density without accurate control of developing time and temperature. This type of developer is particularly suited for the use of certain professional men such as dentists for X-ray development work, since it is only necessary that the negative be placed in the solution and the negative will be developed to produce the same contrast regardless of the time left in the bath, and hence do not require special timing or attention to produce good results. "Monobaths" have been marketed in the form of solutions but are subject to an even greater degree than many developers to the inherently poor keeping qualities of solutions. It is not usually practical for the amateur to make up a "Monobath" from the individual chemicals as even greater care in weighing out and solution is essential with this type of developer than is the case with ordinary developers. The present invention permits the marketing of "Monobaths" in solid form which will keep indefinitely and which require no skill or care in use because it is only necessary to throw the "Monobath" block into the requisite quantity of water and allow it to dissolve.

The blocks may be prepared in various and convenient sizes, such as required for preparing a gallon, half gallon, quart, or pint, of the photographic developing solution.

The blocks of the present invention may be produced by the usual powder molding methods. The ingredients may be either in the powder or crystalline form. However, when the powdered form is used, less pressure is required to mold, but the rate of dissolution is increased. Substances which are inert photographically may be used as binders to aid in molding or to increase the rate of disintegration and dissolution in water. In considering various pressures to be used in the instances as given, it is also necessary to consider the particle size in the molded portion. A structure containing a composition of large particle size generally will disintegrate more rapidly under the stated conditions due to larger interstices offered to the solute.

In the formation of orthodox developer blocks, it usually is not necessary to moisten the ingredients; in some cases it may be necessary to moisten the outside layer. A binding agent, however, can be added in very small quantities to the core, to gain overall structural strength. Such a binding agent as milk sugar may be used, the amount being extremely small.

In the case of a "Monobath" block, a mixture of anhydrous and crystalline thiosulfate can be moistened to obtain a rigid core. Because of the affinity of the anhydrous material for water, a positive heat of solution is formed. This, even in small amounts, permits the formation and escape of gas (air) which in turn forms small channels of escape in the block so formed.

The use of agents to increase solubility have been tested. Thus wetting agents such as so-

dium dioctylsulfosuccinate can be incorporated in very small quantities to any one of the layers to gain this purpose. Sodium dioctylsulfosuccinate has been found beneficial in developer solutions due to its ability to reduce surface tension thereby allowing a shorter or more complete induction period.

The invention will be specifically described with reference to the accompanying drawing in which:

Fig. 1 is an elevation showing the block of material in the form of a sphere;

Fig. 2 is an elevation showing a block of the material in the form of a cube;

Fig. 3 is a vertical section through the center of the sphere of Fig. 1 showing the composition thereof;

Fig. 4 is also a vertical section through the center of the sphere of Fig. 1 showing the composition thereof, and,

Fig. 5 is a vertical section through the center of the sphere of Fig. 1.

The vertical section shown in Fig. 3 represents a form of the invention wherein certain ingredients are combined to form the inner core 1 and a second group of ingredients are combined to form an outer layer 2. For example, the outer layer may contain a mixture of the developer agents and a protective amount of sodium or other sulfite as may be required, and the core contains the necessary alkali, and if desired, buffers, retarders or other ingredients.

Fig. 4 illustrates a form in which a protective coating 3 is employed to preserve the ingredients or prevent the block from chipping.

Fig. 5 represents a more highly perfected form of the invention in which each type of ingredient is molded into a single concentric layer. This form shows an inner core 4 which, for example, may contain the necessary alkali, surrounding which is a layer 5 containing sodium sulfite, which in turn is surrounded by a layer 6 containing the developing agent and if desired a portion of the sulfite, and an outer surrounding layer 7 containing a protective coating of sulfite.

It can be seen that under any conditions of dissolution with a given molded product as illustrated in Figs. 3 and 5 that the outer layers must necessarily dissolve away before the next layer of material is affected. This progressive action assures that solution of the materials will follow a stated and pre-determined order.

The following examples are illustrations of methods by which the invention is carried out in connection with specific developer formulas. However, the particular formulas are used for purposes of illustration only and the invention is not necessarily limited thereto.

In the various formulations, I have described the developer agents as Metol (monomethylparaminophenol sulfate) or hydroquinone (paradi-oxybenzene) or various combinations of them. I do not wish to confine the invention to these particular compounds, but have used them only to serve as satisfactory materials for our use. Other developing agents such as paraphenylenediamine or pyrogallol can also be used in our molded units, and the invention is generally applicable to any developer formula.

Example 1

The following illustrates a selective molded unit for a high-contrast developer of comparatively high energy.

A core mixture, such as is illustrated in Fig. 3 is formed from the following dry ingredients:

	Grams
5 Sodium bisulfite.....	10.20
Sodium hydroxide.....	13.00
Potassium bromide.....	5.00

An outer layer is formed from the following ingredients and is molded onto the core:

	Grams
10 Hydroquinone.....	12.20
Sodium bisulfite.....	2.00

A molded unit formed in such a manner contains the proper ingredients to form 1 liter of developer solution. The purpose of combining the small amount of sodium bisulfite in the outer layer is to prevent a discoloration of the developer agent through aerial oxidation.

Example 2

Fig. 4 shows a more perfected form of the present invention in which a protective layer 3 which may consist of sulfite with or without a binder, surrounds the rest of the developing block. This protective layer performs two functions. In the first place it prevents any aerial oxidation of the underlying layer containing the developing agents. This factor is of importance when the developer is to be kept in damp atmospheres and particularly where high energy developing agents are employed. The second function is that of a shell by the use of a thin layer which may be relatively hard and strong particularly where a binder is used, or where the sulfite is moistened before molding. In this way it is possible to compress the other layers of the block much more lightly so that they remain in a form which will dissolve rapidly. Nevertheless the hard outer protective shell will give the block sufficient strength for storage and handling.

Example 3

A medium high contrast developer of medium-energy may be prepared as follows:

A core mixture, such as illustrated in Fig. 3 is formed from the following ingredients:

	Grams
50 Sodium sulfite.....	36.0
Sodium carbonate.....	20.0
Potassium bromide.....	1.5

An outer layer is formed by the following ingredients and is molded onto the core:

	Grams
55 Metol.....	8.00
Hydroquinone.....	5.00
Sodium sulfite.....	4.00

A molded unit formed in such a manner contains the proper ingredients to form 1 liter of developer solution. The sodium sulfite is combined in the outer layer to reduce the effect of aerial oxidation, which would otherwise discolor the material.

Example 4

A medium energy "Monobath" block may be prepared as follows:

A core mixture such as is illustrated in Fig. 5 is prepared from the following ingredients:

	Grams
75 Sodium thiosulfate, 5H ₂ O.....	37.50
Anthranilic acid or guanidine anthranilate.....	5.00

An intermediate layer is formed from the following ingredients and molded onto the core:

	Grams
Guanidine carbonate.....	27.00
Sodium sulfite.....	36.00

An outer layer is formed from the following ingredients and molded thereto:

	Grams
Metol.....	8.00
Hydroquinone.....	5.00

A final thin protective layer of sodium sulfite, 4 grams, may then be molded as a protection against aerial oxidation.

A unit such as this contains the proper ingredients to form 1 liter of "Monobath" solution.

The present invention has been described particularly in connection with typical developers of silver halide material as the problem of solution of developers in a predetermined order is particularly acute in this field. However, the invention is not limited broadly to developers for silver halides as other multi-component developers such as for example in the use of the diazo type process, are preferably produced by solution of the components in a predetermined order. Such developers may also be prepared in solid form according to the present invention.

What I claim is:

1. A multi-component photographic developer composition the components of which require solution in a predetermined order in the form of a solid mass comprising a core containing the component which is last to be dissolved surrounded by at least one layer containing components requiring solution before the component of the core.
2. A silver halide developer composition in the form of a solid mass comprising a core containing alkali surrounded by at least one layer containing a photographic developing agent.
3. A composition for use in silver halide development comprising a molded solid mass of the alkali surrounded by at least one concentric layer of a mixture of the developing agent and a sulfite.
4. A composition in the form of a block for use in silver halide development comprising an inner core comprising a mixture of an alkali, a sulfite and a restrainer surrounded by at least one layer of a mixture of a photographic developer and a sulfite.
5. A solid molded composition for use in combined developing and fixing of silver halide material comprising an inner core containing a fixing agent and a delayed action chemical surrounded by a series of concentric layers, the first containing alkali and at least one further layer containing developing agent and sulfite, each layer being of substantially uniform thickness.
6. A solid molded composition for use in combined developing and fixing of silver halide material comprising an inner core containing a fixing agent and an anthranilic acid compound surrounded by a series of concentric layers, the first containing alkali and at least one further layer containing developing agent and sulfite, each layer being of substantially uniform thickness.
7. A solid molded composition for use in combined developing and fixing of silver halide material comprising an inner core containing a fixing agent and guanidine anthranilate surrounded by a series of concentric layers, the first containing alkali and at least one further layer con-

aining developing agent and sulfite, each layer being of substantially uniform thickness.

3. A developer according to claim 2 in which the developing agents are Metol and hydroquinone.

9. A developer according to claim 5 in which the developing agents are Metol and hydroquinone.

10. A photographic developer composition according to claim 2 in which an outer protective

layer is provided in the form of a relatively hard shell and the inner layers are in the form of lightly pressed granular material.

11. A photographic developer composition according to claim 5 in which an outer protective layer is provided in the form of a relatively hard shell and the inner layers are in the form of lightly pressed granular material. 5

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