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(54) Package for photographic chemicals.

(57) A package for solid photographic processing chemicals which comprises at least one bag which has been made from hydroxyethyl cellulose, wherein the sum of the contents of the bag or bags based on the amount of chemicals to provide a working strength solution of 1000ml is not more than 100g of chemicals and of which in the case of a solid developer composition not more than 50g of sodium sulphite and/or potassium carbonate may be present and of which in the case of a solid fixer composition not more than 70g of ammonium thiosulphate may be present.

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This invention relates to packages for photographic chemicals.

Photographic chemicals for use in processing exposed photographic material are usually sold either as solids which require to be weighed out and then dissolved in water or as concentrated solutions of chemicals which are then diluted to produce the required concentration. However, powdered chemicals require handling and efforts are being made to cut down the production of fine chemical particles which are sure to be formed when powdered chemicals are weighed out or added to water. On the other hand, it is expensive to transport concentrated chemical solutions because of the weight of water being transported.

Efforts have been made to prepare photographic chemicals as mixed solid lumps of the correct proportions so that the correct amount is cut-off the lump to prepare for example 1000ml of working strength solution. However, in spite of adding wetting agents, expanding agents and other excipients to aid in the dissolution of the solid chemical lumps this method has not proved to be satisfactory.

Increasing use is being made of water-soluble polyvinyl alcohol bags into which solid water-soluble chemicals are packed. These bags containing solid chemicals are then placed in the requisite quantity of water to provide a solution of the required strength. We have attempted to use polyvinyl alcohol bags in which to pack solid photographic chemicals which are then placed in water to yield a photographic processing solution of the requisite strength. However, in some cases the bags did not dissolve at all whilst in other cases initially the bags appeared to dissolve but after a few minutes a dense precipitate was observed in the solution which thus could not be used for photographic processing.

We have found a method of packing photographic chemicals in water soluble bags in which the above listed disadvantages have been obviated.

Therefore according to the present invention there is provided a package for photographic solid processing chemicals which comprises at least one bag made from hydroxyethyl cellulose, wherein the sum of the contents of the bag or bags based on the amount of chemicals to provide a working strength solution of 1000ml is not more than 100g of chemicals and of which in the case of developing chemicals not more than 50g of sodium sulphite and/or sodium or potassium carbonate may be present and of which in the case of a solid fixer composition not more than 70g of ammonium thiosulphate may be present.

It is to be understood that these figures relate to a composition to make 1000ml of working strength solution. If the package is for a lesser or a greater volume these figures must be adjusted mutatis mutandis.

If these figures are exceeded the bag or bags will not dissolve and/or a cloudy solution is obtained.

Often in the case of solid developer composition it is required to use two bags, one containing the developing agents and the other containing the remainder of the composition.

Preferably the hydroxyethyl cellulose used to prepare the bags comprise from 1 to 10% by weight of a water-soluble plasticiser.

Suitable water-soluble plasticisers are polyols and polyalkylene oxide derivatives. An especially suitable plasticiser is a polyethylene glycol which has a molecular mass of from 150 to 500.

The effect of the plasticiser is threefold. Firstly it renders the bag more flexible. Secondly it renders the bag heat sealable, thirdly it helps in the dissolution of the bag.

Preferably the thickness of the bag, and the amount of plasticiser present in the polymer from which the bag is composed are so chosen that the bag dissolves in water at 20 °C in less than 5 minutes and preferably in from 1 to 2 minutes, providing that the thickness of the bag is sufficient to enable the bag to be picked-up without it rupturing.

Preferably the thickness of the bag is from 10 to 120μm and most preferably from 30-60μm.

Hydroxy ethyl cellulose may be obtained by treating cellulose with sodium hydroxide and then reacting it with ethylene oxide. Hydroxy ethyl groups are introduced into the chain of anhydroglucose units which form the cellulose chain. Each anhydrocellulose unit has three reactive hydroxyl groups. The average number of moles of ethylene oxide that become attached to each anhydroglucose unit in the cellulose chain is called moles of substituent combined or M.S. The higher the M.S. the greater the water solubility of the hydroxy ethyl cellulose. However it is difficult and expensive to obtain a hydroxy ethyl cellulose with an M.S. of 3. A particularly useful hydroxy ethyl cellulose for use in the present invention has an M.S. of 2.5, and this is extremely water-soluble. An example of such a hydroxy ethyl cellulose is Natrosol 250 which is manufactured by and the registered trade mark of Hercules Incorporated. Clear films can be cast from this compound.

The dimensions of the bag depend on the weight of the chemicals required to prepare 1000ml of the working strength solution.

The following Example will serve to illustrate the invention.

Example

Preparation of bags.

1.8g of Natrosol 250 LR grade Hydroxyethyl cellulose (as supplied by Hercules) and 0.2g of polyethylene glycol having a molecular mass of 200 were added to 98g of water at 20 °C. This mixture was stirred and the pH of the mixture was adjusted to 10.0 by the addition of a small quantity of 4M sodium hydroxide. After 2 minutes stirring a clear colourless solution was obtained. This solution was poured onto a 10 inch by 6 inch glass plate and by use of a glass rod on even coating on the glass plate was obtained. The glass plate was heated to 50 °C over a hot plate. After 120 minutes all the water had evaporated from the glass plate to give flexible tough film of 45 microns thickness which weighed 2.0g.

The film was folded-over and the two opposing edges were heat-sealed to form an open-ended bag. Into this bag was placed a photographic paper developing composition having the following ingredients herein after referred to as composition 1.

sodium sulphite	5.4g
diethylene triamine pentacetic acid	2g
sodium ascorbate	30g
4 methyl-4 hydroxymethyl-1-phenyl-3 pyrazolidinone	2.5g
potassium carbonate	30g
potassium bromide	3.3g

The open end was then heat sealed to form an enclosed sachet of the developer composition.

This sachet was then added to 1000ml of water at 25 °C. With gentle stirring the bag and the chemicals contained therein dissolved to yield a colourless clear solution in 3 minutes.

This solution was used to develop thirty 10" x 8" sheets of exposed photographic black and white paper comprising a standard silver chlorobromide emulsion. The sensitometric results were compared with the results obtained using the same formulation developer which had been prepared using the same chemicals straight from their respective containers.

No difference was found in the sensitometric results obtained. This showed that the presence of the dissolved hydroxy ethyl cellulose and polyethylene glycol in the developer solution had no photographic effect on the exposed photographic material during development.

A number of other bags were prepared similarly.

Other compositions packed in these bags were:-

2. Rapid powder fix which comprised	
ammonium thiosulphate	98g
sodium metabisulphite	16g
packed in one bag	

3. Film fix	
sodium thiosulphate	104g
sodium metabisulphite	16g

4. Paper fixer	
ammonium thiosulphate	65g
sodium metabisulphite	0.7g

5. Film developer		
bag A	(hydroquinone (metol	5g 2g
bag B	(sodium sulphite (borax (sodium tripolyphosphate	100g 3g 3.5g

6. Colour developing composition		
Potassium bromide sodium tripoly phosphate sodium carbonate sodium metabisulphite sodium sulphite	1.05g) 3.5g) 28.g) 1.5g) 3.0g)	Bag A
Colour developing agent hydroxylamine sulphite	2.38g) 2g)	Bag B

7. 'One shot' film developer		
sodium sulphite sodium carbonate stabiliser	5g) 2.5g) 0.012g)	Bag A
Hydroquinone 4 methyl-4 hydroxymethyl-1 phenyl-3 pyrazolidinone Ascorbic acid Diethylene triamine pentaacetic acid	0.61g) 0.2g) 1g) 2g)	Bag B

Each of these packages were placed in water at 20 °C and the water was stirred. The results were as follows.

Composition	Bag dissolution	Colour of solution
1	complete	clear in 3 mins
2	bag did not dissolve	
3	bag did not dissolve	
4	bag dissolved very slowly (50 minutes)	
5	bag A dissolved, bag B did not dissolve	
6	both bags dissolved	clear in 3 mins
7	both bags dissolved	clear in 3 mins

The bags which do not dissolve formed a sticky mass which rendered the solution useless for photographic use. As a comparison bags were prepared from polyvinyl alcohol.

3.6g of polyvinyl alcohol which was made from polyvinyl acetate which had been 88.0% hydrolysed and which had a molecular mass of 10,000, was mixed with 0.4g of polyethylene glycol having a molecular mass of 200. This mixture was dissolved in 96g of water at 30 °C. After 10 minutes stirring a clear colourless solution was obtained. 30g of this solution was poured onto a 4 inch x 8 inch glass plate and by use of a glass rod an even coating on the glass plate was obtained. The glass plate was heated to 50 °C over a hot plate. After 120 minutes all the water had evaporated from the glass plate to give a flexible tough film of 40 microns thickness which weighed 1.20g.

The film was folded-over and the two opposing edges were heat-sealed to form an open-ended bag. Into this bag was placed a photographic paper developing composition having the following ingredients herein after referred to as composition 1 as hereinbefore set forth and also paper fixer of composition 4.

The open ends of each bag was then heat sealed to form an enclosed sachet of in one case developer composition and in the other case fixer composition.

These sachets were then added to 1000ml of water at 25 °C and the water then stirred.

In the case of the sachet which comprised developer composition 1 the bag dissolved within minutes but after 15 minutes a heavy precipitate appeared.

In the case of the sachet which comprised fixing composition 4 the bag appeared to dissolve after 1 hour but then a heavy precipitate was observed.

Thus neither of these solutions could be used to process photographic material.

It is to be understood that in this Example the bags have been hand made and the bags filled by hand. In practice the bags are cast in bulk and they are filled in an automatic filling plant with the operators not coming into contact with the powdered chemicals. The packages are packed in boxes from which the photographic laboratory or end user picks up a bag or bags and dissolves it or them in water to prepare a working strength solution of the required composition without coming into contact with the powdered chemicals at all.

Claims

1. A package for solid photographic processing chemicals which comprises at least one bag which has been made from hydroxyethyl cellulose, characterised in that the sum of the contents of the bag or bags based on the amount of chemicals to provide a working strength solution of 1000ml is not more than 100g of chemicals and of which in the case of a solid developer composition not more than 50g of sodium sulphite and/or sodium or potassium carbonate may be present and of which in the case of a solid fixer composition not more than 70g of ammonium thiosulphate may be present.

2. A package according to claim 1 characterised in that the hydroxyethyl cellulose used to prepare the bags comprises from 1 to 10% by weight of a water-soluble plasticiser.

3. A package according to claim 2 characterised in that the plasticiser is a polyol or a polyethylene oxide.

4. A package according to claim 3 characterised in that the polyol is a polyethylene glycol which has a molecular mass of from 150 to 500.

5. A package according to claim 1 characterised in that the photographic chemicals are a fixer composition packed in one bag.

6. A package according to claim 1 characterised in that the photographic chemicals are a developing composition packed in one bag.

7. A package according to claim 1 characterised in that the photographic chemicals are developing composition, the developing agents being present in one bag and the remainder of the composition being present in a second bag.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 93 10 4841

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	EP-A-0 469 877 (KONICA) * page 3, line 40 - line 56 * * page 5, line 17 - line 27 *	1-7	G03C5/26
A	JP-A-1 024 900 (SANKI SHOKUHIN) * abstract * * page 2, left column, line 31 - line 32 *	1-7	
A	EP-A-0 444 230 (AICELLO CHEMICAL) * page 7; table 1 * * claims 1,6 *	1-7	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	27 MAY 1993	MAGRIZOS S.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
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P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
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& : member of the same patent family, corresponding document

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