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(54) **Method of recovering a photographic addendum from a dispersion thereof.**

(57) A water-insoluble organic photographic addendum is recovered from a dispersion of a mixture thereof and an oil-former in an aqueous medium containing a hydrophilic colloid and a surface active agent by adding a selected oleophilic non-ionic surface active agent.

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METHOD OF RECOVERING A PHOTOGRAPHIC ADDENDUM FROM A DISPERSION THEREOF

This invention relates to a method of recovering a photographic addendum from a dispersion thereof.

It is often necessary to incorporate a water-insoluble organic compound into a hydrophilic colloid layer of a photographic sheet material (which may or may not be light-sensitive) in such a way that the compound cannot diffuse within or away from that layer. For example, in a colour photographic material having superimposed red-, green- and blue-sensitive gelatino-silver halide emulsion layers containing, respectively, cyan, magenta and yellow dye-forming couplers it is essential that these couplers remain in their respective layers. If they do not, the image produced in each layer is not of the appropriate pure subtractive primary colour but is of a mixture of dyes giving unwanted absorption.

One method which has been employed for preventing diffusion of an incorporated organic compound in a hydrophilic colloid layer comprises dispersing the compound in admixture with a high-boiling, water-immisible, organic solvent. Such a solvent, which need not be liquid at room temperature, is often referred to, and is referred to herein, as an 'oil-former' (see for instance United Kingdom patent specification No. 541,589). This method is carried out by dispersing the mixture of organic compound and oil-former in an aqueous solution of the hydrophilic colloid with the aid of a surface active agent and subsequently mixing the dispersion so obtained with the other constituents of the coating composition to be used in forming the layer. If,

through being stored too long or for other reasons, a dispersion does not have the required characteristics, it is desirable to recover the dispersed compound therefrom so that it may be reused.

A method which has been proposed for recovering water-insoluble photographic addenda from dispersions thereof in aqueous media containing a proteinaceous colloid and a surface active agent, comprises treating the dispersion with an enzyme to degrade the colloid, and a substance which causes precipitation of the addendum (see Research Disclosure September 1977, Item No. 16101). In the case where an ionic surface active agent is present, the substance causing precipitation may be a surface active agent of opposite charge. Whilst this method is capable of giving satisfactory results with coupler and other dispersions, it has the disadvantage of employing an enzyme which must be eliminated completely from the recovered addendum to prevent degradation of any colloid in which the addendum is subsequently to be dispersed.

According to the present invention there is provided a method of recovering a water-insoluble organic compound from a dispersion of a mixture thereof with an oil-former in an aqueous medium containing a hydrophilic colloid and a surface active agent, which comprises adding to the liquid dispersion an oleophilic non-ionic surface active agent so as to cause crystallization of the organic compound.

The method of the invention is very suitable for the recovery of couplers and other compounds (such as redox dye-releasing compounds) used for image formation in colour photographic materials from their dispersions, and is also useful for recovering such other organic compounds as ultraviolet absorbers and dye stabilizing agents.

References giving information on couplers are given in Section VII of Research Disclosure December 1978, Item 17643.

The couplers commonly employed in photographic materials are water-insoluble compounds often containing ballast groups, phenolic (including naphtholic) couplers being used for producing cyan dyes and compounds containing an activated methylene group, including both heterocyclic and open-chain compounds, being used for producing magenta and yellow dyes. Important magenta couplers are pyrazolones and important yellow couplers are benzoylacetanilides. Patents describing couplers include the following United States Patents:

Cyan dye-forming

2 367 531	3 034 892
2 423 730	3 311 476
2 474 293	3 419 390
2 772 162	3 458 315
2 895 826	3 476 563

Magenta dye-forming

2 343 703	3 062 653
2 369 489	3 127 269
2 600 788	3 311 476
2 908 573	3 419 391
2 933 391	3 518 429

Yellow dye-forming

2 298 443	3 277 155
2 407 210	3 408 194
2 875 057	3 415 652
2 908 573	3 447 928
3 265 506	3 933 501

An account of dye-forming development is given in 'Modern Photographic Processing', Vol. 2, Grant Haist, Wiley, New York, 1978, Chapter 9.

A great variety of compounds may be used as oil-formers in coupler dispersions, as described in United Kingdom Patent Specification No. 541,589. The compounds are substantially water-insoluble, high-boiling organic crystalloidal materials. Particularly suitable are esters, including organic esters such as di-n-butyl phthalate, and phosphate esters, such as tricresyl phosphate. The oil-former preferably has a boiling point of at least 150°C and is chemically inert in the chosen system. Other desirable properties are listed in the U.K. Specification, together with numerous examples of suitable compounds.

The non-ionic surface-active agent used in a method of the invention is oleophilic and preferably has a hydrophile-lipophile balance (HLB) value no greater than 5 but having such a value does not necessarily ensure that an agent will be satisfactory. Methods of determining HLB are described in, for instance, 'Emulsion Science', P.Sherman, Academic Press, London (1968), Chapter 3. In many instances, the HLB of commercially available surface active agents is quoted by the suppliers. It may be noted that the maximum HLB value likely to be found for any surface active agent is approximately 40.

Types of surface active agent which have been found effective for the method of the invention include:

glycerol esters
polyoxyethylene ethers
sorbitan esters.

Commercial surface active agents of these types include certain of the agents sold under the trade marks:

'Arlacel',
'Brij',
'Emerest',
'Grindtek',

'Pluriol',
'Pluronic',
'Span'.

For a given dispersion, it is necessary to select an optimum non-ionic surface active agent and the optimum concentration thereof, by preliminary testing with small quantities. A mixture of non-ionic surface active agents may in some cases give a synergistic effect. The amount of non-ionic surface active agent required is of the same order as the amou t of addendum and oil-former in the dispersion. Thus the weight of surfactant required is usually from 0.1 to 10 times the total weight of addendum and oil-former.

In some instances, the extraction of the compound to be recovered can be facilitated by addition either of a slightly water soluble organic solvent of the kind sometimes referred to as an 'auxiliary solvent' (see, for instance, U.K. Patent No. 791,219). Examples of auxiliary solvents are ethyl and butyl acetates, and 2-(2-butoxyethoxy)ethyl acetate.

In carrying out a method of the invention, the dispersion is if necessary liquified by melting and the non-ionic surface active agent added. Any auxiliary solvent to be used may be added at the same time or later. It is convenient when an auxiliary solvent is used to dissolve the surface active agent in this.

After the compound to be recovered has crystallised, it may be filtered and washed with warm

water to remove the hydrophilic colloid and any water soluble surface-active agent. It may also be washed with an organic solvent having a low solvent power for the compound being recovered but a high solvent power for the oleophilic surface active agent. Hydrocarbon solvents such as petroleum ether, hexane and heptane are suitable in many instances. Often, the dried recovered compound is sufficiently pure for reuse without further treatment.

The invention is illustrated by the following Examples:

Example 1

A 10 g sample of each of two coupler dispersions was melted and made up to a volume of 30 ml with distilled water. Each dispersion had the approximate composition:

coupler	100 g
oil-former	50 g
gelatin	100 g
anionic surfactant*	see table below
other constituents and water to make	1000 g

*a sodium naphthalene sulphonate.

The couplers, oil-formers and weights of anionic surfactant in the two dispersions were as follows:

Dispersion A

Cyan dye-forming coupler:		2-[α-(2,4-di-tert-amyl-phenoxy)-butyramido]-4,6-dichloro-5-methylphenol.
Oil former:	:	dibutylphthalate.
Weight of anionic surfactant	:	3.5 g.

Dispersion B

Magenta dye-forming coupler	:	1-(2,4,6-trichlorophenyl)-3-{5-[α-3-tert-butyl-4-hydroxyphenoxy)tetradecane-amido]-2-chloroanilino}-5-pyrazolone.
Oil former	:	tricresylphosphate
Weight of anionic surfactant:		5.0 g.

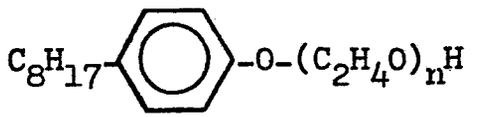
A 1 ml quantity of a solution of 1 volume of the surfactant 'Pluronic L121' (trade mark) in two volumes of 2-(2-butoxyethoxy)ethyl acetate was stirred in.

'Pluronic L121' is believed to have the structure:

$$HO(CH_2CH_2O)_a(\underset{CH_3}{CHCH_2O})_b(CH_2CH_2O)_cH$$

wherein (a + c) is approximately 10 and b is approximately 70, and has an HLB of about 0.5.

The dispersion was held at 50°C for ten minutes and then 4 ml of the surface active agent 'Triton X-100', believed to have the structure:



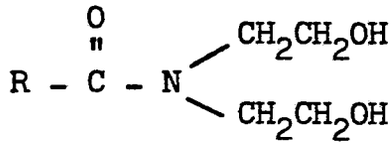
was added. The mixture was diluted to 120 ml, held at 50°C for 1 hour and the recovered coupler then filtered off and washed with water. In each case the recovery rate was 80% and the coupler recovered was at least as pure as that used in preparing the original dispersion.

Example 2

Twenty grams of a dispersion of the magenta dye dye-forming coupler 1-(4,6-dichloro-2-methoxyphenyl)-3-[α-(3-n-pentadecylphenoxy)butyramido]-5-pyrazolone, this dispersion having the approximate composition:

coupler	100 g
oil-former (tricresylphosphate)	50 g
gelatin	100 g
anionic surfactant ('Alkanol XC')	3 g
other constituents and water to make	1000 g

was mixed with 20 g of water and with 4 g of a mixture of 2 g 'Witcamide 511' (trade mark) and 2 g of 10% aqueous solution of 'Alkanol XC' (trade mark). 'Witcamide 511' is a non-ionic surface active agent believed to be of the formula:



wherein R is a long-chain fatty acid group of 12 to 18 carbon atoms. 'Alkanol XC' is believed to be sodium triisopropyl naphthalene sulphonate. The mixture obtained was stirred at 50°C for 8 hours and the precipitated coupler filtered off and washed successively with hot water and heptane. The coupler was recovered in 57% yield and was at least

as pure as when incorporated into the original dispersion (measured by high pressure liquid chromatography).

This method was repeated on a multi-kilogram scale, the only changes in procedure being that when crystallization was complete (as judged by microscopic examination) a volume of heptane equal to the volume of 'Witcamide' used was added and the mixture then stirred for a further 3 hours before the recovered coupler was filtered off and washed, the yield and the purity of the product were at least as satisfactory as for the small scale trial.

Example 3

This is a comparative Example.

The effectiveness of two cationic surface active agents at causing crystallisation of coupler from the dispersions A and B used for Example 1 was examined. The cationic agents were:

(i) cetyl pyridinium chloride

(ii) didodecyldimethylammonium bromide.

In each test, 10 ml of a 1% w/v aqueous solution of the cationic agent was added to 4 ml of the dispersion and held at 40°C. Samples were examined after 2 and 24 hours using a microscope at X200 magnification and with crossed polarizing filters. The numbers and sizes of crystals observed are expressed qualitatively in the following table.

Time:-	2 hours			24 hours		
Cationic surfactant:-	none	i	ii	none	i	ii
Dispersion A	few small	many small	none	many small	very many	many
Dispersion B	few small	none	none	few small	some large	none

The dispersion A sample treated with cationic surfactant (i) for 24 hours was filtered and the coupler crystals collected represented a recovery of less than 25%.

It is evident that even the more effective of the cationic surfactants was slower and less efficient than an oleophilic non-ionic surfactant as required for the method of the present invention.

CLAIMS

1. A method of recovering a water-insoluble organic compound from a dispersion of a mixture thereof with an oil-former in an aqueous medium containing a hydrophilic colloid and a surface active agent, which comprises adding to the liquid dispersion an oleophilic non-ionic surface active agent so as to cause crystallization of the organic compound.

2. A method according to claim 1 wherein the non-ionic surface-active agent is a glycerol ester, polyoxyethylene ether or sorbitan ester.

3. A method according to claim 1 or 2 wherein a second non-ionic surface-active agent is added to the dispersion.

4. A method according to any of the preceding claims wherein the water-insoluble organic compound to be recovered is a dye-forming coupler.

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European Patent Office

EUROPEAN SEARCH REPORT

Application number
EP 81 30 3984

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
	GB - A - 1 274 048 (BAYER) * Claims 1-3 * --	1-3
	DE - A - 2 706 550 (BETZ INTERNATIONAL) * Page 2, lines 1-7; page 2, last paragraph; claims 1-4 * --	1-3
A	GB - A - 2 003 856 (FUJI PHOTO FILM) ----	

CLASSIFICATION OF THE APPLICATION (Int Cl.³)

G 03 C 11/24
G 03 C 7/32
B 01 D 17/04

TECHNICAL FIELDS SEARCHED (Int. Cl.³)

G 03 C 11/24
7/32
C 09 B 67/00
B 01 D 17/04
13/00
21/00
21/01

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	23-11-1981	PHILOSOPH