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(54) **High contrast photographic materials containing microcrystal dispersions of hydrazines.**

(57) A negative acting photographic material capable of producing a high contrast image comprising a photographic silver halide emulsion in association with a water-insoluble hydrazine in the form of microcystals having a mean particle size of not more than 10 microns, preferably 0.05 to 5 microns. The microcrystals may be in the photographic silver halide emulsion or in a layer adjacent thereto.

EP 0 326 433 A2

Description

HIGH CONTRAST PHOTOGRAPHIC MATERIALS CONTAINING MICROCRYSTAL DISPERSIONS OF HYDRAZINES

This invention relates to negative acting silver halide photographic materials and in particular to high contrast photographic materials containing water-insoluble hydrazines.

Hydrazines find a variety of uses in silver halide photography. They have been used in negative working surface latent image forming silver halide emulsions to increase speed and/or contrast. They have been used in direct positive internal latent image forming emulsions as nucleating agents such as those described in US Patent Specification No. 3227552 and reviewed in Research Disclosure No. 235 (1983) item 23510.

The most effective hydrazines employed in silver halide photographic systems possess a combination of substituents to balance activity and stability. The stability of hydrazines is increased by attaching directly to one of the nitrogen atoms a tertiary carbon atom, such as the carbon atom of an aromatic ring. The art has long recognised that the activity of these stabilised hydrazines can be advantageously modified by the direct attachment of an acyl group to the remaining nitrogen atom. Thus, the most commonly employed hydrazines are 1-acyl-2-arylhydrazines.

Silver halide emulsions and/or developers containing hydrazines are disclosed, for example, in United States patent Specifications Nos. 2419975, 2563785, 3227552, 3386831, 3730727, 4030925, 4031127, 4080207, 4168977, 4224401, 4243739, 4243739, 4245037, 4255511, 4266013, 4272614, 4276364, 4323643, 4478928 and British Patent Specifications Nos. 1560005, 1579956, 2034908A and 2066492B.

US Patent Specification No. 2419975 discloses that high contrast negative images are obtained in silver halide photographic emulsions by the addition of hydrazine compounds. However, a highly alkaline developer is required having a pH of approximately 12.8, this is very susceptible to air oxidation and is too unstable to be stored or used for long periods. Subsequent research has developed alternative hydrazines which allow a lowering of pH to reduce adverse effects incurred by aerial oxidation of the developer.

US Patent Specification No. 4168977 discloses the use of a hydrazine with the formula:

$R^1NHNHCHO$

in which:

R^1 represents an aryl group, in combination with silver chlorobromide or silver chlorobromoiodide emulsions. This combination is capable of functioning at a lower pH than the hydrazines of US Patent No. 2419975 and a pH of 11.5 is exemplified.

US Patent Specification No. 4224401 discloses the use of a hydrazine of the formula:

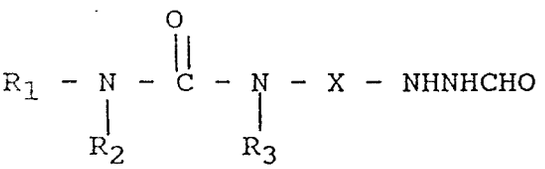
$R^1NHNHCOR^2$

in which:

R^1 is an aryl group; and

R^2 is a hydrogen atom, C1 to C3 alkyl or phenyl optionally substituted with substituents which are preferably electron withdrawing, in combination with silver bromide or silver iodobromide emulsions. This combination is also functional at a pH lower than that disclosed in US Patent No. 2419975 and a pH of 11.5 is exemplified when R^2 is hydrogen.

US Patent Specification No. 4323643 discloses silver halide photographic emulsions containing a hydrazine of the general formula:



in which:

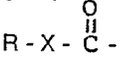
R^1 and R^2 each represents hydrogen, an aliphatic group, an aromatic, or a heterocyclic group;

R_3 represents hydrogen or an aliphatic group, and

X represents a divalent aromatic group.

Light sensitive silver halide photographic materials containing these types of hydrazines are stated to provide high-contrast negative images and good dot image quality.

US Patent Specification No. 4560638 discloses the use of a related class of arylhydrazines in which the aryl group is substituted by a group of the formula:

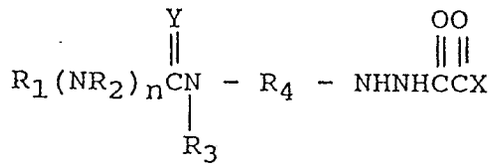


in which:

one of X and X^1 represents N-H, the other represents a divalent chalcogen and R represents an aliphatic or aromatic residue. The use of these compounds is said to give improved dot quality and low levels of pepper

fog.

European Patent Publication No. 217310 discloses contrast promoting agents of the formula:



in which:

X represent NR_5R_6, or OR_7;

R_1 and R_2 independently represent hydrogen, substituted or unsubstituted alkyl, haloalkyl, hydroxyalkyl, alkoxyalkyl, alkylaminoalkyl or arylalkyl having up to 18 carbons; cycloalkyl; phenyl or naphthyl; alkylphenyl, cyanophenyl, halophenyl or alkoxyphenyl substituents;

R_3 represents hydrogen, benzyl, alkoxybenzyl, halobenzyl or alkylbenzyl, provided that if neither R_1 nor R_2 is hydrogen, then R_3 is hydrogen;

R_4 represents a divalent aromatic group which may be substituted or unsubstituted;

R_5, R_6 and R_7 independently represent hydrogen, alkyl, hydroxylalkyl, haloalkyl, alkoxyalkyl, alkylaminoalkyl, acylaminoalkyl, aminoalkyl or phenylalkyl having up to 12 carbons; a cycloalkyl substituent; phenyl or naphthyl; an alkylphenyl, cyanophenyl halophenyl or alkoxyphenyl substituent.

Additionally, either R_1 and R_3 or R_1 and R_2 can be linked to form a heterocyclic ring system containing 3 to 10 atoms. Also R_5 and R_6 can be linked to form a heterocyclic ring system containing 3 to 10 atoms.

Y represents an oxygen or sulphur atom. If Y is sulphur then n = 1, if Y is oxygen then n = 0 or 1.

A further class of hydrazines for use in high contrast silver halide photographic systems is disclosed in European Patent Publication No. 253665A. The hydrazides are of the general formula:

$R^3 - NR^4 - NR^5 - G - X$

in which;

R^3 represents an aryl group,

one of R^4 and R^5 is a hydrogen and the other is selected from hydrogen, aryl sulphonyl and trifluoroacetyl,

G represents carbonyl, sulphonyl, sulphoxy, phosphoryl or an N-substituted or unsubstituted imino group and

X is a moiety such that at a pH in the range of 9.5 to 12.5 in the presence of an oxidised hydroquinone a cyclisation reaction takes place cleaving the moiety -G-X from the remainder of the molecule and forming a cyclic structure comprising atoms of the moiety -G-X.

In general the hydrazines referred to above have limited solubility in water. In order to incorporate them into photographic elements the hydrazines have been treated by techniques used for the addition of other additives to photographic emulsion. The hydrazine is typically dissolved in a solvent selected from organic solvents compatible with water, eg. alcohols, glycols, ketones, esters, amides and the like which exert no adverse influences on the photographic characteristics, and the solution is added to the photographic elements. The hydrazines have also been added to photographic emulsion in oil dispersions by methods used when water-insoluble (so-called oil soluble) couplers are added to emulsions. For example, US Patent Specification No. 2419974 discloses a method of dissolving the water insoluble hydrazines in water immiscible organic solvents and dispersing this solution into water which may contain dispersing or wetting agents and gelatin, this dispersion then being added to a suitable gelatin silver halide emulsion.

US Patent Specification No. 4474872 discloses a process of adding a dispersion of a substantially water-insoluble photographic additive to a photographic emulsion. The dispersion is prepared by mechanically grinding and dispersing the photographic additive in a form of fine grain having a size of 1 micron or less in an aqueous system adjusted to a pH value of 6 to 8 and controlled to a temperature of 60 to 80°C. The additive is included in the photographic emulsion without the need of an organic solvent. The photographic additives disclosed include spectral sensitising dyes, antifoggants, colour couplers, dyes, sensitizers, hardeners, ultraviolet absorbing agents, antistatic agents, brightening agents, desensitizers, developers, discolourisation inhibitors and mordants. There is no disclosure of the use of this method for the addition of hydrazines.

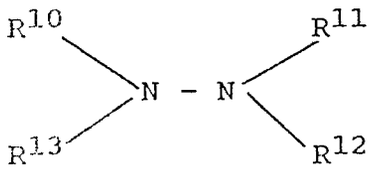
It has now been found that water-insoluble hydrazine compounds may be advantageously incorporated into photographic silver halide emulsions in the form of an aqueous dispersion of microcrystals.

According to the present invention there is provided a negative acting photographic silver halide material capable of producing a high contrast image comprising a photographic silver halide emulsion in association with a water-insoluble hydrazine in which the water-insoluble hydrazine is present as microcrystals having a mean particle size of not more than 10 microns distributed through the photographic silver halide emulsion, or in a layer adjacent thereto.

It has been unexpectedly found that the use of a dispersion of hydrazine may provide improved sensitometric properties, improved dot quality and improved coating quality compared with the use of oil dispersions of the same hydrazine and organic solutions of the hydrazine. This discovery is in contrast to the teaching of US Patent Specification No. 2419974 and is not predicted in the general teaching of the art.

The hydrazines employed in the invention are water-insoluble i.e. they possess a solubility of less than 0.1% in water at 20° C. The hydrazines may be selected from any of the water insoluble hydrazines known in the art and many examples will be found in the literature cited hereinbefore.

In general the hydrazines will be of the general formula:



in which:

R^{10} represents an aliphatic, aromatic or heterocyclic group and

R^{11}, R^{12} and R^{13} independently represent hydrogen or an aliphatic, aromatic or heterocyclic group.

Preferred hydrazines are of the general formula:

R^{14} - NR^{15} - NR^{16} - G - X

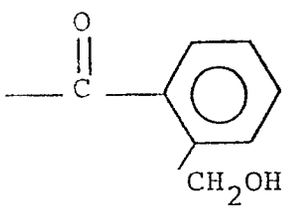
in which;

R^{14} represents an aryl group,

one of R^{15} and R^{16} is a hydrogen and the other is selected from hydrogen, aryl sulphonyl and trifluoroacetyl,

G represents carbonyl, sulphonyl, sulphoxy, phosphoryl or an N-substituted or unsubstituted imino group and

X is hydrogen, alkyl, aryl or a moiety such that at a pH in the range of 9.5 to 12.5 in the presence of an oxidised hydroquinone a cyclisation reaction takes place cleaving the moiety -G-X from the remainder of the molecule and forming a cyclic structure comprising atoms of the moiety -G-X. Particularly preferred hydrazines are those in which -G-X represents:



Examples of such hydrazines are disclosed in European Patent Publication No. 253665A.

The dispersions of hydrazines may be prepared by mechanical attrition of solid hydrazine in an aqueous medium by means of a colloid mill or similar device or preferably by mixing a solution of the hydrazine in a water miscible solvent with an aqueous medium under conditions of rapid agitation such that rapid precipitation of the hydrazine as a finely divided solid dispersion occurs. Suitable water miscible solvents are, for example, acetone, tetrahydrofuran (THF), dimethylformamide, dimethylsulphoxide or N-methyl-2-pyrrolidone.

The aqueous medium in which the hydrazine is dispersed preferably contains a water soluble polymer such as gelatin and/or a surfactant in order to assist and stabilise uniform dispersion of the solid hydrazine.

The presence of any water immiscible compounds (so called oils) gives disadvantageous properties in terms of speed, contrast and half tone dot quality.

The dispersion technique allows a relatively narrow distribution of hydrazine crystallite sizes to be reproducibly made generally within the range of mean particle size of 0.01 to 10 microns, typically 0.05 to 1.0 microns, for subsequent addition to the gelatin silver halide emulsion. Generally, at least 95% of the particles have a particle size of less than 10 microns, preferably less than 5 microns, most preferably less than 1 micron. Any large particles formed (greater than 10 microns) may be removed by filtration.

Whilst the formation of a well characterised solid dispersion of hydrazine prior to addition to the silver halide is preferred, an alternative procedure is to add a solution of hydrazines in a water miscible solvent under conditions which lead to precipitation of essentially pure microcrystals of solid hydrazine directly in the emulsion.

The formation of a reproducible crystallite size is of importance as in some cases the addition of an organic solvent solution of very water insoluble hydrazines to the silver halide emulsion can lead to coagulation. Presumably the conditions of the dispersions are such that a controlled precipitation is occurring with the subsequent stabilisation of the crystallites being maintained by the presence of gelatin and the surfactants that are present. This is unlike the case of the so called oil dispersions where the hydrazines are dissolved in the oil droplets which are themselves stabilised by the gelatin and any surfactants or other ingredients present. We have found that these different preparations of the hydrazide dispersions lead to different and

advantageous properties being conferred on the silver halide emulsion to which it is added.

In order to measure the mean particle size of the hydrazines a sedimentation field flow fractionation technique may be used. The results from this equipment assume that the particles are spherical, although in reality some may be needle-shaped. From the graph of number of particles against particle diameter the mean particle size and dispersity of distribution can be assessed. Because of approximations which may have to be made relative to the refractive index of the particles (and density if a weight distribution is plotted) the results may vary by ±50% relative to the true value.

Alternatively, microscopy may be used to assess the particle distribution.

It has been found that some hydrazines have needle-shaped particles while others more closely approximate to spheres.

The invention will now be illustrated by the following Example.

Example 1

The details of the 0.25 micron silver bromochloride emulsion coating formulation used are:
(per mole of silver halide)

Dye 40ml of 1% green sensitising dye anhydro-5,5′-dichloro-9,ethyl-3,3′-bis(3-sulphopropyl)oxacarbocyanine.

Polyethylene oxide compound 150ml of 1% Brij 58 (polyoxyethylene (20) cetyl ether)

Surfactant 10ml of 10% Hostapur SAS93 (a secondary alkane sulphonate sodium salt commercially available from Hoechst AG)

Contrast Promoter 30ml of 5% benzhydrol in methanol

Hardener 25ml/litre of top coat of a 10% 1-hydroxy-3,5-dichlorotriazine solution

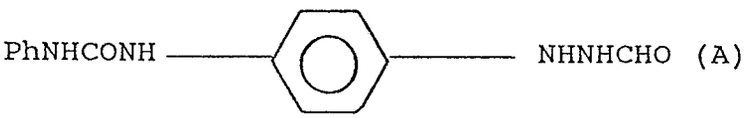
The above mixture was then coated together with a hydrazine formulation onto a polyester base having suitable antihalation backing. A triazine hardened gelatin top coat was also employed. The resulting coatings were then processsed in the standard fashion as follows. The elements were exposed using an exposing device having a tungsten filament source with the light attenuated by a neutral density graduated filter in order to assess speed and contrast. Similar exposures were made through a Kodak "Ultratec" half-tone screen to assess dot quality. Development was achieved using a suitable high contrast developer having the following formulation:

Water	1800g
Potassium hydroxide	195g
Potassium metabisulphite	124g
Diethylenetriaminepentaacetic acid 5Na	10g
Pyruvic acid sodium salt	7.5g
Hydroquinone	60g
Metol (p-methylaminophenol)	5.0g
5-Methylbenzotriazole	0.2g
Potassium bromide	9.25g
Potassium chloride	2.7g
Phosphoric acid (85%)	90g
Final Volume	2.0 litres
	pH 11.0

The coatings were evaluated for quality of coating, speed, contrast and half tone dot quality.

The experiments that were carried out consisted of adding one of the following hydrazine (A or B) solutions or dispersions to the emulsion prior to coating.

In one series of experiments the hydrazine used was



(A)

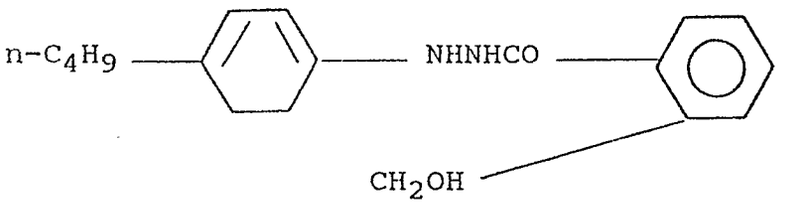
Formulation:

A1. 1% solution of hydrazine (A) in dimethylformamide

A2. A dispersion made by slow jetting of a 3% DMF solution of the hydrazine (A) at room temperature into a gelatin solution at 40°C comprising 10g gel, 3g 10% Hostapur SAS93 and water to 100g. The dispersion was achieved using a Sylverson Company "Laboratory Homogeniser".

A3. As A2 except the hydrazine solution consisted of 0.6g of hydrazine (A) in 15ml of dimethylformamide and 4ml N,N-diethyldodecanamide (oil).

A similar series of coatings were made with the following solutions or dispersions of the hydrazine:



(B)

Formulation:

B1. 2% solution of hydrazine (B) in dimethylformamide

B2. 5g of hydrazine (B) dissolved in 100ml dimethylformamide at room temperature and dispersed into 30g of gelatin dissolved in 960g of deionised water and 13.3g 10% Maprofix Type 563 (sodium lauryl sulphate, commercially available from Onyx Chemical Company) at 40°C. The dispersion was achieved by a Sylverson Laboratory Homogeniser.

B3. As B2 except 5ml of N,N-diethyldodecanamide oil was added to the dimethylformamide solution.

The quantities were adjusted so that 3g of hydrazine was added per mole of silver halide. The solubilities of hydrazines A and B in water were found to be less than 0.1% at 20°C.

The dispersions A2 and B2 were obtained by running the Sylverson Homogeniser at full speed and allowing the hydrazine solution to slowly run into the gelatin/surfactant solution, typically at 20ml/minute. The hydrazine solution entered the aqueous solution by means of tube arranged such that its orifice lay near the homogeniser head. At the end of addition the homogeniser was allowed to run for a further minute. After this the dispersion was allowed to stand to reduce the amount of foam present. Filtration then gave a ready to use dispersion.

When viewed under an optical microscope the crystallites of the hydrazine could be seen in the host gelatin matrix and the grain size assessed.

The sensitometric results and coating qualities obtained are given in Table 1. Table 1 also includes a subjective comparison of the half tone dots produced by exposing the film through an Eastman Kodak grey "Ultratec" screen and a continuous tone wedge, the film then being processed in the standard manner.

TABLE 1

Hydrazine Formulation	Relative Log Speed	Contrast 1	Contrast 2	D_{min}	Coating* Quality	Dot* Quality
A1	1.92	3.2	20	0.04	3	1
A2	2.18	9.7	32	0.03	1	1
A3	2.03	1.4	2	0.04	5	4
B1	2.13	2.4	20	0.06	3	1
B2	1.96	1.6	24	0.05	1	1
B3	1.85	1.9	4	0.06	5	4

Contrast 1 is the contrast between 0.07 and 0.17 above fog

Contrast 2 is the contrast between 0.05 and 2.5 above fog

* The assessment of coating quality and dot quality was made using a scale of 1(best) to 5(worst).

It can be seen that the best results were obtained from the dispersion in a gelatin solution without any oil being present (A2 and B2). Addition of a dimethylformamide solution tended to give irreproducible results and very poor coating quality. This can be ascribed to the insoluble nature of the hydrazine which precipitates on

addition to the silver halide emulsion giving large crystallites, these in turn lead to rough poor quality coatings. The sensitometric results are in part dependent on the size and nature of the hydrazine crystallites.

The results obtained from using an oil dispersion (A3 and B3) are also very poor; the presence of the oil inhibits the infectious development effect giving very low contrast and sensitivity.

The dispersion into a gelatin solution containing surfactant can be achieved from a variety of organic solvents such as dimethylformamide and dimethylsulphoxide as well as tetrahydrofuran and methanol in the case of hydrazine B; however, dimethylformamide is preferred from a practical point of view. In this way an essentially monodisperse crystallite dispersion of mean particle size around 0.1-0.2 microns was produced in the case of hydrazine B. In order to remove any particularly large particles of hydrazine the dispersion can be filtered.

The particle size distribution of hydrazine B in the dispersion resulting from B2 is shown in the accompanying drawing which shows the normalised number of crystallites as a function of their size as measured by the sedimentation field flow fractionation technique.

The crystallites of hydrazine A resulted from A2 were found to have a mean particle size of approximately 5 microns (determined by measuring particle diameters by microscopy).

Claims

1. A negative acting photographic silver halide material capable of producing a high contrast image comprising a photographic silver halide emulsion in association with a water-insoluble hydrazine characterised in that the water-insoluble hydrazine is present as microcrystals having a mean particle size of not more than 10 microns distributed through the photographic silver halide emulsion or in a layer adjacent thereto.

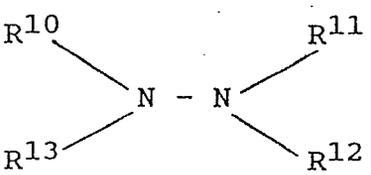
2. A negative acting photographic silver halide material as claimed in Claim 1 characterised in that the hydrazine is distributed through the silver halide photographic emulsion.

3. A negative acting photographic silver halide material as claimed in Claim 1 characterised in that at least 95% of the microcrystals have a particle size less than 10 microns.

4. A negative acting photographic silver halide material as claimed in Claim 2 characterised in that at least 95% of the microcrystals have a particle size less than 5 microns.

5. A negative acting photographic silver halide material as claimed in any preceding claim characterised in that the microcrystals have a mean particle size in the range 0.05 to 1.0 micron.

6. A negative acting photographic silver halide material characterised in that the hydrazine is of the general formula



in which:
R^{10} represents an aliphatic, aromatic or heterocyclic group and
R^{11}, R^{12} and R^{13} independently represent hydrogen or an aliphatic, aromatic or heterocyclic group, or
R^{14} - NR^{15} - NR^{16} - G - X
in which;
R^{14} represents an aryl group,
one of R^{15} and R^{16} is a hydrogen and the other is selected from hydrogen, aryl sulphonyl and trifluoroacetyl,
G represents carbonyl, sulphonyl, sulphoxy, phosphoryl or an N-substituted or unsubstituted imino group and
X is hydrogen, alkyl, aryl or a moiety such that at a pH in the range of 9.5 to 12.5 in the presence of an oxidised hydroquinone a cyclisation reaction takes place cleaving the moiety -G-X from the remainder of the molecule and forming a cyclic structure comprising atoms of the moiety -G-X.

7 . A method of preparing a photographic material as defined in any preceding claim comprising coating a high contrast photographic silver halide emulsion on a support characterised in that an aqueous dispersion of water-insoluble hydrazine having microcrystals of a mean particle size of no more than 10 microns is formed and either incorporated in the photographic silver halide emulsion prior to coating or coated in a layer adjacent the photographic silver halide emulsion.

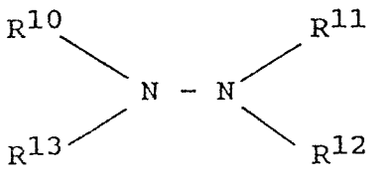
8. A method as claimed in Claim 7 characterised in that the dispersion of water-insoluble hydrazine having a particle size of no more than 10 microns is formed in an aqueous medium comprising a water soluble polymer and optionally silver halide in the absence of immiscible solvents.

9. A method as claimed in Claim 8 characterised in that the dispersion is formed by contacting a solution of hydrazine in a water miscible organic solvent with an aqueous medium containing a water-soluble polymer and optionally a surfactant and/or silver halide and mechanically dispersing the microcrystals formed.

10. A method as claimed in any one of Claims 7 to 9 characterised in that at least 95% of the microcrystals have a particle size less than 10 microns.

11. A method as claimed in any one of Claims 7 to 10 characterised in that the microcrystals have a mean particle size in the range 0.05 to 1.0 micron.

12. A method as claimed in any one of Claims 7 to 11 characterised in that the hydrazine is of the general formula



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in which;
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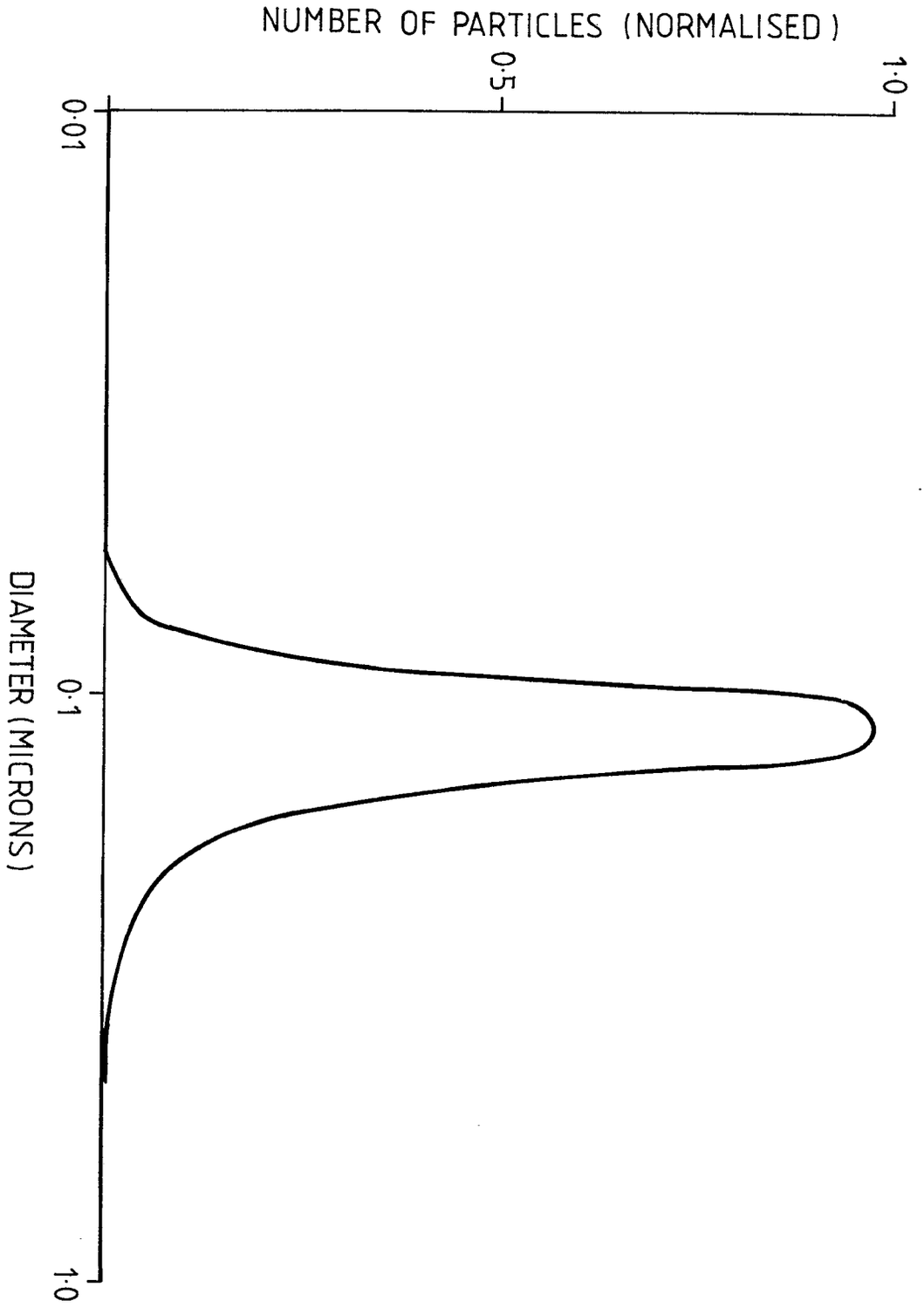
G represents carbonyl, sulphonyl, sulphoxy, phosphoryl or an N-substituted or unsubstituted imino group and
X is hydrogen, alkyl, aryl or a moiety such that at a pH in the range of 9.5 to 12.5 in the presence of an oxidised hydroquinone a cyclisation reaction takes place cleaving the moiety -G-X from the remainder of the molecule and forming a cyclic structure comprising atoms of the moiety -G-X.


NUMBER OF PARTICLES (NORMALISED)
0·5
1·0
0·01
0·1
1·0
DIAMETER (MICRONS)