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(71) Applicant: **EASTMAN KODAK COMPANY**
343 State Street
Rochester, New York 14650-2201(US)

(72) Inventor: **Loblaw, John Calvin, c/o Eastman Kodak Company**
343 State Street
Rochester, New York 14650-2201(US)
Inventor: **Tsaur, Allen Keh-Chang, c/oEastman Kodak Company**
343 State Street
Rochester, New York 14650-2201(US)
Inventor: **Kam-Ng, Mamie, c/oEastman Kodak Compa**
343 State Street
Rochester, New York 14650-2201(US)

(74) Representative: **Brandes, Jürgen, Dr. rer. nat. et al**
Wuesthoff & Wuesthoff, Patent- und Rechtsanwälte, Schweigerstrasse 2
W-8000 München 90(DE)

(54) **An improved phototypesetting paper.**

(57) A phototypesetting paper is disclosed comprised of a white reflective support and an imaging layer unit coated on the support exhibiting a maximum density of at least 2.0 and a contrast in excess of 2.0 over a 0.75 log E exposure range measured from the minimum exposure required to produce a density of 0.2 above fog. The imaging layer unit is comprised of a tabular grain silver halide emulsion having a grain halide content of from 0 to 5 mole percent chloride, from 0 to 15 mole percent iodide and from 80 to 100 mole percent bromide, based on total silver.

The phototypesetting paper is characterized in that the coefficient of variation of the tabular grain emulsion is less than 15 percent, based on the total grain population of the emulsion having an equivalent circular diameter of greater than 0.1 μm, and greater than 97 percent of the total grain population of the emulsion having an equivalent circular diameter of greater than 0.1 μm is accounted for by tabular grains having a mean thickness of less than 0.2 μm and a tabularity of greater than 25.
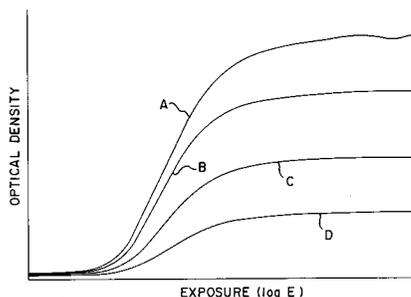
FIG. 1

The invention relates to photography. More specifically, the invention relates to an improved photographic paper.

Brief Description of the Drawings

Figure 1 is a plot of optical density versus exposure for varied silver coverages.

Figure 2 is a plot of optical density versus exposure for the same emulsion with and without a contrast increasing dopant.

Figure 3 is a photomicrograph of a conventional tabular grain emulsion.

Figures 1 to 6 inclusive are characteristic curves obtained by plotting optical density as a function of exposure over an exposure range of 3.9 log E in increments of 0.15 logE, where E is exposure measured in lumen (meter-candle) seconds.

Phototypesetting paper is a photographic product intended to produce black, maximum density silver images on a white, minimum density background. The image is viewed by reflection from a white support. Common reference to the reflective supports as "paper" supports is a historical legacy from an earlier era in which the supports were in fact entirely paper. Today white reflective plastics are commonly present to supplement or even entirely supplant paper in the reflective support.

To obtain the impression of a black image on a white background it is necessary that exposed areas exhibit a density of at least 2.0, that unexposed area exhibit a uniform low density, typically less than 0.1, and that there be a sharp transition between exposed and unexposed areas. The maximum density of 2.0 has been selected by the art, since it is not possible to distinguish densities greater than 2.0 in viewing a reflection print. The minimum density of less than 0.1 is a conveniently realized fog level. To have a sharp transition between exposed and unexposed area (that is, for the eye not to pick out areas of intermediate density), phototypesetting papers are normally constructed with a contrast of at least 2.0.

The selection of silver halide emulsion layer units to be coated on the reflective support is dictated by these density and contrast requirements. Maximum density and contrast requirements dictate the silver halide coating coverages for a selected emulsion. Referring to Figure 1, a series of characteristic curves are shown identically produced by the same silver halide emulsion coated on the same support, but at varied silver halide coating coverages. The emulsions were coated on a film support, to permit the full range of maximum densities to be measured. Curves B, C and D represent silver halide coating coverages of 75, 50 and 25 percent, respectively, that of Curve A. It is apparent that maximum density and contrast decrease with each progressive decrease in the silver halide coating coverage.

How much silver halide must be coated per unit area to produce a particular maximum image density depends upon the covering power of the emulsion. Covering power is commonly defined as the maximum image density divided by developed silver per unit area, typically reported in units of g/m^2 or mg/dm^2.

Although tabular grains had been observed in silver bromide and bromoiodide photographic emulsions dating from the earliest observations of magnified grains and grain replicas, it was not until the early 1980's that photographic advantages, such as improved speed-granularity relationships, increased covering power both on an absolute basis and as a function of binder hardening, more rapid developability, increased thermal stability, and improved image sharpness in monolayer formats, were realized to be attainable from silver halide emulsions in which the majority of the total grain population based on grain projected area is accounted for by tabular grains satisfying the mean tabularity relationship:

$$D/t^2 > 25$$

where

D is the equivalent circular diameter (ECD) in micrometers of the tabular grains and
t is the thickness in micrometers of the tabular grains.

Because of their increased covering power high ($D/t^2 > 25$) tabularity emulsions were immediately put to use in phototypesetting paper. Wilgus et al U.S. Patent 4,434,226 (note col. 54, line 58, through col. 56, line 21) and Kofron et al U.S. Patent 4,439,520 (note col. 74, line 31, through col. 75, line 62) report the same comparison of a phototypesetting paper prepared with a high tabularity emulsion and a conventional, low tabularity emulsion. In the comparison the high tabularity emulsion produced a higher maximum density with a lower silver coverage. By referring to Figure 1, it is apparent that a still larger reduction in silver coverages could have been realized at equal maximum densities. A recent sample of a commercial phototypesetting paper tabular grain emulsion revealed a mean ECD of 2.1 μm, a mean tabular grain thickness of 0.087 μm, and a COV of 43 percent.

Notwithstanding their early application in phototypesetting paper tabular grain emulsions were not

ideally suited for this application. The reason for this is that when coated at a silver coverage sufficient to produce a maximum density of 2.0 the emulsions still exhibited a contrast of less than 2.0. This was overcome by a well-known contrast enhancing procedure of incorporating a contrast enhancing dopant (specifically, rhodium) in the tabular grains. Such dopants have the disadvantage of reducing photographic speed. This is illustrated in Figure 2. Characteristic Curves E and F are identically produced, except that the emulsion used to form Curve F was rhodium doped. Whereas both curves exhibit the same maximum density, the contrast of Curve E is well below that of Curve F. However, the improvement in contrast in Curve F is realized by a large reduction in speed, evidenced by the increase in exposure required to initiate the formation of densities above fog.

In the earliest tabular grain emulsions dispersity concerns were largely focused on the presence of significant populations of nonconforming grain shapes among the tabular grains conforming to an aim grain structure. Fig. 3 is a photomicrograph of an early high aspect ratio tabular grain silver bromoiodide emulsion first presented by Wilgus et al and Kofron et al to demonstrate the variety of grains that can be present in a high aspect ratio tabular grain emulsion. While it is apparent that the majority of the total grain projected area is accounted for by tabular grains, such as grain 101, nonconforming grains are also present. The grain 103 illustrates a nontabular grain. The grain 105 illustrates a fine grain. The grain 107 illustrates a nominally tabular grain of nonconforming thickness. Rods, not shown in Figure 3, also constitute a common nonconforming grain population in tabular grain silver bromide and bromoiodide emulsions.

While the presence of nonconforming grain shapes in tabular grain emulsions has continued to detract from achieving narrow grain dispersities, as procedures for preparing tabular grains have been improved to reduce the inadvertent inclusion of nonconforming grain shapes, interest has increased in reducing the dispersity of the tabular grains. Only a casual inspection of Fig. 3 is required to realize that the tabular grains sought themselves exhibit a wide range of equivalent circular diameters.

A technique for quantifying grain dispersity that has been applied to both nontabular and tabular grain emulsions is to obtain a statistically significant sampling of the individual grain projected areas, calculate the corresponding ECD of each grain, determine the standard deviation of the grain ECDs, divide the standard deviation of the grain population by the mean ECD of the grains sampled and multiply by 100 to obtain the coefficient of variation (COV) of the grain population as a percentage. While very highly monodisperse (COV < 10 percent) emulsions containing regular nontabular grains can be obtained, even the most carefully controlled precipitations of tabular grain emulsions have rarely achieved a COV of less than 20 percent. Research Disclosure, Vol. 232, August 1983, Item 23212 (Mignot French Patent 2,534,036, corresponding) discloses the preparation of silver bromide tabular grain emulsions with COVs ranging down to 15. Research Disclosure is published by Kenneth Mason Publications, Ltd., Dudley Annex, 21a North Street, Emsworth, Hampshire P010 7DQ, England.

Saitou et al U.S. Patent 4,797,354 reports in Example 9 a COV of 11.1 percent; however, this number is not comparable to that reported by Mignot. Saitou et al is reporting only the COV within a selected tabular grain population. Excluded from these COV calculations is the nonconforming grain population within the emulsion, which, of course, is the grain population that has the maximum impact on increasing grain dispersity and overall COV. When the total grain populations of the Saitou et al emulsions are sampled, significantly increased COVs result. In a remake of the Example 9 emulsion of Saitou et al a COV of 21.3 percent was observed when COV was based on the total grain population.

In one aspect, this invention is directed to a phototypesetting paper comprised of a white reflective support and an imaging layer unit coated on the support exhibiting a maximum density of at least 2.0 and a contrast in excess of 2.0 over a 0.75 log E exposure range measured from the minimum exposure required to produce a density of 0.2 above fog. The imaging layer unit is comprised of a tabular grain silver halide emulsion having a grain halide content of from 0 to 5 mole percent chloride, from 0 to 15 mole percent iodide and from 80 to 100 mole percent bromide, based on total silver.

The phototypesetting paper is characterized in that the coefficient of variation of the tabular grain emulsion is less than 15 percent, based on the total grain population of the emulsion having an equivalent circular diameter of greater than 0.1 μm, and greater than 97 percent of the projected area of the total grain population of the emulsion having an equivalent circular diameter of greater than 0.1 μm is accounted for by tabular grains having a mean thickness of less than 0.2 μm and a tabularity of greater than 25.

It has been discovered that when a phototypesetting paper is constructed using a tabular grain emulsion substantially free of nontabular grains and having thin (<0.2 μm), high (>25) tabularity, and highly monodisperse (COV<15%) tabular grains a variety of advantages can be realized as compared to conventional phototypesetting papers containing tabular grain emulsions. Higher speeds and contrasts are observed when compared with similarly constructed phototypesetting papers in which the tabular grains exhibit only conventional coefficients of variation. Especially striking are the increased contrasts observed in

the shoulder region of the characteristic curve, which ranges from maximum density to an optical density of about 0.4 below maximum density. Reduced granularity has also been observed.

The invention is directed to an improved phototypesetting paper. The phototypesetting paper is comprised of a conventional white reflective support and an imaging layer unit coated on the support exhibiting a maximum density of at least 2.0 and a contrast in excess of 2.0 over a 0.75 log E exposure range measured from the minimum exposure required to produce a density of 0.2 above fog.

The phototypesetting paper employs in the imaging layer unit an emulsion containing tabular grains having a mean thickness of less than 0.2 μm and a mean tabularity of greater than 25. These emulsions, which contain thin tabular grains and exhibit high tabularities, provide the high levels of silver covering power that have rendered tabular grain emulsions particularly attractive for use in phototypesetting papers.

This invention improves the properties of phototypesetting papers containing thin, high tabularity tabular grain emulsions by employing tabular grain emulsions prepared by novel processes that (1) increase the proportion of the total grain population accounted for by thin tabular grains and (2) increase the mon-odispersity of the total grain population forming the imaging layer unit. The phototypesetting paper of the invention exhibits a coefficient of variation of the tabular grain emulsion that is less than 15 percent (preferably less than 10 percent), based on the total grain population of the emulsion having an equivalent circular diameter of greater than 0.1 μm. The low coefficient of variation of the total grain population having an equivalent circular diameter of greater than 0.1 μm is made possible by producing an emulsion in which the tabular grain population accounts for all or very nearly all (greater than 97 percent and optimally greater than 98 percent) of the total projected area of grains having an equivalent circular diameter of greater than 0.1 μm and by reducing the dispersity observed within the tabular grain population itself. The phototypeset-ting papers employ in their emulsion layer units high tabularity, thin tabular grain silver halide emulsions that consist essentially of tabular grains and minimum or near minimum coefficients of variations, based on the total grain population having an equivalent circular diameter of greater than 0.1 μm.

As precipitated by the procedures disclosed below, there are only negligible quantities present of grains having equivalent circular diameters of 0.1 μm or less. However, it is recognized that it is conventional practice in preparing emulsions for phototypesetting papers to blend in small quantities of small diameter grains (sometimes referred to as "dust") to adjust the profile of the characteristic curve. These small grains can range up to 0.1 μm in size, but are typically Lippmann emulsions having mean grain equivalent circular diameters of about 0.05 μm. Grains of up to 0.1 μm in equivalent circular diameter are too small to participate to any significant degree in light capture or light scattering within the visible spectrum. The role of these blended small grain components, when present, is more analogous to image modifiers than to that of the imaging grain population.

The phototypesetting papers of this invention have been realized by the discovery and optimization of novel processes for the precipitation of tabular grain emulsions of reduced grain dispersities. These processes are capable of preparing emulsions suited for phototypesetting paper use having a grain halide content of from 0 to 5 mole percent chloride, from 0 to 15 (preferably 0 to 5) mole percent iodide and from 80 to 100 (preferably 90 to 100) mole percent bromide, based on total silver. The grain population can consist essentially of silver bromide as the sole silver halide. Silver bromide is incorporated in the grains during both grain nucleation and growth. Silver iodide and/or silver chloride can also be present in the grains, if desired. The presence of iodide is particularly beneficial to increasing emulsion speed when present in even very small amounts, such as $\geq$0.1 mole percent, based on silver. However, higher levels of iodide produce warmer image tones that are preferably avoided. It is therefore preferred to limit iodide to less than 5 mole percent (optimally less than 3 mole percent) based on silver.

Grain populations consisting essentially of tabular grains having mean thicknesses in the range of from 0.080 to 0.2 μm and mean tabularities (as defined above) of greater than 25 are well within the capabilities of the precipitation procedures set forth below. These ranges permit any mean tabular grain ECD to be selected appropriate for the photographic application. In other words, the present invention is compatible with the full range of mean ECDs of conventional tabular grain emulsions. A mean ECD of about 10 μm is typically regarded as the upper limit for photographic utility. For most applications the tabular grains exhibit a mean ECD of 5 μm or less. Since increased ECDs contribute to achieving higher mean aspect ratios and tabularities, it is generally preferred that mean ECDs of the tabular grains be at least about 0.4 μm.

Any mean tabular grain aspect ratio within the mean tabular grain thickness and tabularity ranges indicated is contemplated. Mean tabular grain aspect ratios for the tabular grains preferably range from 5 to 100 or more. This range of mean aspect ratios includes intermediate (5 to 8) and high (>8) average aspect ratio tabular grain emulsions. For the majority of photographic applications mean tabular grain aspect ratios in the range of from about 10 to 60 are preferred.

While mean aspect ratios have been most extensively used in the art to characterize dimensionally

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tabular grain emulsions, mean tabularities (D/t^2, as defined) provide an even better quantitative measure of the qualities that set tabular grain populations apart from nontabular grain populations. The emulsions of the invention contain exhibit tabularities of greater than 25. Typically mean tabularities of the tabular grain emulsions range up to about 500. Since tabularities are increased exponentially with decreased tabular grain mean thicknesses, extremely high tabularities can be realized ranging up to 1000 or more.

The emulsions contemplated for use have been made available by the discovery and optimization of improved processes for the preparation of tabular grain emulsions by (a) first forming a population of grain nuclei, (b) ripening out a portion of the grain nuclei in the presence of a ripening agent, and (c) undertaking post-ripening grain growth. Minimum COV coprecipitated grain population emulsions consisting essentially of tabular grains satisfying the requirements of this invention has resulted from the discovery of specific techniques for forming the population of grain nuclei.

To achieve the lowest possible grain dispersities the first step is undertake formation of the silver halide grain nuclei under conditions that promote uniformity. Prior to forming the grain nuclei bromide ion is added to the dispersing medium. Although other halides can be added to the dispersing medium along with silver, prior to introducing silver, halide ions in the dispersing medium consist essentially of bromide ions.

The balanced double jet precipitation of grain nuclei is specifically contemplated in which an aqueous silver salt solution and an aqueous bromide salt are concurrently introduced into a dispersing medium containing water and a hydrophilic colloid peptizer. One or both of chloride and iodide salts can be introduced through the bromide jet or as a separate aqueous solution through a separate jet. It is preferred to limit the concentration of chloride and/or iodide to the overall levels described above or less during grain nucleation. Silver nitrate is the most commonly utilized silver salt while the halide salts most commonly employed are ammonium halides and alkali metal (e.g., lithium, sodium or potassium) halides. The ammonium counter ion does not function as a ripening agent since the dispersing medium is at an acid pH--i.e., less than 7.0.

Instead of introducing aqueous silver and halide salts through separate jets a uniform nucleation can be achieved by introducing a Lippmann emulsion into the dispersing medium. Since the Lippmann emulsion grains typically have a mean ECD of less than 0.05 μm, a small fraction of the Lippmann grains initially introduced serve as deposition sites while all of the remaining Lippmann grains dissociate into silver and halide ions that precipitate onto grain nuclei surfaces. Techniques for using small, preformed silver halide grains as a feedstock for emulsion precipitation are illustrated by Mignot U.S. Patent 4,334,012; Saito U.S. Patent 4,301,241; and Solberg et al U.S. Patent 4,433,048.

The low COV emulsions contemplated for use can be prepared by producing prior to ripening a population of parallel twin plane containing grain nuclei in the presence of selected surfactants. Specifically, it has been discovered that the dispersity of the tabular grain emulsions of this invention can be reduced by introducing parallel twin planes in the grain nuclei in the presence of one or a combination of polyalkylene oxide block copolymer surfactants. Polyalkylene oxide block copolymer surfactants generally and those contemplated for use in preparing the emulsions of this invention in particular are well known and have been widely used for a variety of purposes. They are generally recognized to constitute a major category of nonionic surfactants. For a molecule to function as a surfactant it must contain at least one hydrophilic unit and at least one lipophilic unit linked together. A general review of block copolymer surfactants is provided by I.R. Schmolka, "A Review of Block Polymer Surfactants", J. Am. Oil Chem. Soc., Vol. 54, No. 3, 1977, pp. 110-116, and A.S. Davidsohn and B. Milwidsky, Synthetic Detergents, John Wiley & Sons, N.Y. 1987, pp. 29-40, and particularly pp. 34-36.

One category of polyalkylene oxide block copolymer surfactant found to be useful in the preparation of the emulsions is comprised of two terminal lipophilic alkylene oxide block units linked by a hydrophilic alkylene oxide block unit accounting for at least 4 percent of the molecular weight of the copolymer. These surfactants are hereinafter referred to category S-I surfactants.

The category S-I surfactants contain at least two terminal lipophilic alkylene oxide block units linked by a hydrophilic alkylene oxide block unit and can be, in a simple form, schematically represented as indicated by diagram I below:

(I)

| LAO1	HAO1	LAO1
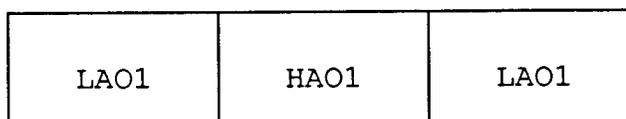
where

LAO1 in each occurrence represents a terminal lipophilic alkylene oxide block unit and

HAO1 represents a linking hydrophilic alkylene oxide block unit.

It is generally preferred that HAO1 be chosen so that the hydrophilic block unit constitutes from 4 to 96 percent of the block copolymer on a total weight basis.

It is, of course, recognized that the block diagram I above is only one example of a polyalkylene oxide block copolymer having at least two terminal lipophilic block units linked by a hydrophilic block unit. In a common variant structure interposing a trivalent amine linking group in the polyalkylene oxide chain at one or both of the interfaces of the LAO1 and HAO1 block units can result in three or four terminal lipophilic groups.

In their simplest possible form the category S-I polyalkylene oxide block copolymer surfactants are formed by first condensing ethylene glycol and ethylene oxide to form an oligomeric or polymeric block repeating unit that serves as the hydrophilic block unit and then completing the reaction using 1,2-propylene oxide. The propylene oxide adds to each end of the ethylene oxide block unit. At least six 1,2-propylene oxide repeating units are required to produce a lipophilic block repeating unit. The resulting polyalkylene oxide block copolymer surfactant can be represented by formula II:

$$\text{(II)}$$

$$\underset{\text{HO}-(\underset{|}{\overset{CH_3}{CH}}CH_2O)_x-(CH_2CH_2O)_y-(CH_2\underset{|}{\overset{CH_3}{CHO}})_{x'}-\text{H}}{}$$
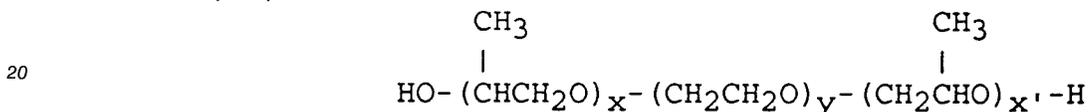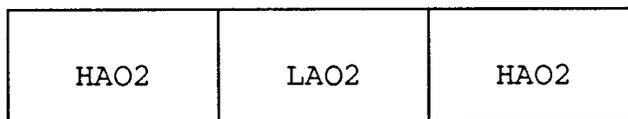
where

x and x' are each at least 6 and can range up to 120 or more and

y is chosen so that the ethylene oxide block unit maintains the necessary balance of lipophilic and hydrophilic qualities necessary to retain surfactant activity. It is generally preferred that y be chosen so that the hydrophilic block unit constitutes from 4 to 96 percent by weight of the total block copolymer. Within the above ranges for x and x', y can range from 2 to 300 or more.

Generally any category S-I surfactant block copolymer that retains the dispersion characteristics of a surfactant can be employed. It has been observed that the surfactants are fully effective either dissolved or physically dispersed in the reaction vessel. The dispersal of the polyalkylene oxide block copolymers is promoted by the vigorous stirring typically employed during the preparation of tabular grain emulsions. In general surfactants having molecular weights of less than about 16,000, preferably less than about 10,000, are contemplated for use.

In a second category, hereinafter referred to as category S-II surfactants, the polyalkylene oxide block copolymer surfactants contain two terminal hydrophilic alkylene oxide block units linked by a lipophilic alkylene oxide block unit and can be, in a simple form, schematically represented as indicated by diagram III below:

(III)	HAO2	LAO2	HAO2

where

HAO2 in each occurrence represents a terminal hydrophilic alkylene oxide block unit and

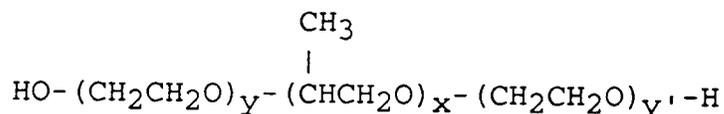LAO2 represents a linking lipophilic alkylene oxide block unit.

It is generally preferred that LAO2 be chosen so that the lipophilic block unit constitutes from 4 to 96 percent of the block copolymer on a total weight basis.

It is, of course, recognized that the block diagram III above is only one example of a category S-II polyalkylene oxide block copolymer having at least two terminal hydrophilic block units linked by a lipophilic block unit. In a common variant structure interposing a trivalent amine linking group in the polyakylene oxide chain at one or both of the interfaces of the LAO2 and HAO2 block units can result in three or four terminal hydrophilic groups.

In their simplest possible form the category S-II polyalkylene oxide block copolymer surfactants are formed by first condensing 1,2-propylene glycol and 1,2-propylene oxide to form an oligomeric or polymeric

block repeating unit that serves as the lipophilic block unit and then completing the reaction using ethylene oxide. Ethylene oxide is added to each end of the 1,2-propylene oxide block unit. At least thirteen (13) 1,2-propylene oxide repeating units are required to produce a lipophilic block repeating unit. The resulting polyalkylene oxide block copolymer surfactant can be represented by formula IV:

$$(IV)$$

$$HO-(CH_2CH_2O)_y-(\overset{\overset{\displaystyle CH_3}{\displaystyle |}}{CHCH_2O})_x-(CH_2CH_2O)_{y'}-H$$
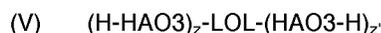
where

x is at least 13 and can range up to 490 or more and

y and y' are chosen so that the ethylene oxide block units maintain the necessary balance of lipophilic and hydrophilic qualities necessary to retain surfactant activity. It is generally preferred that x be chosen so that the lipophilic block unit constitutes from 4 to 96 percent by weight of the total block copolymer; thus, within the above range for x, y and y' can range from 1 to 320 or more.

Any category S-II block copolymer surfactant that retains the dispersion characteristics of a surfactant can be employed. It has been observed that the surfactants are fully effective either dissolved or physically dispersed in the reaction vessel. The dispersal of the polyalkylene oxide block copolymers is promoted by the vigorous stirring typically employed during the preparation of tabular grain emulsions. In general surfactants having molecular weights of less than about 30,000, preferably less than about 20,000, are contemplated for use.

In a third category, hereinafter referred to as category S-III surfactants, the polyalkylene oxide surfactants contain at least three terminal hydrophilic alkylene oxide block units linked through a lipophilic alkylene oxide block linking unit and can be, in a simple form, schematically represented as indicated by formula V below:

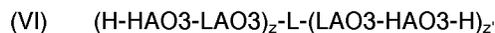(V) $(H-HAO3)_z-LOL-(HAO3-H)_{z'}$

where

HAO3 in each occurrence represents a terminal hydrophilic alkylene oxide block unit,

LOL represents a lipophilic alkylene oxide block linking unit,

z is 2 and

z' is 1 or 2.

The polyalkylene oxide block copolymer surfactants employed can take the form shown in formula VI:

(VI) $(H-HAO3-LAO3)_z-L-(LAO3-HAO3-H)_{z'}$

where

HAO3 in each occurrence represents a terminal hydrophilic alkylene oxide block unit,

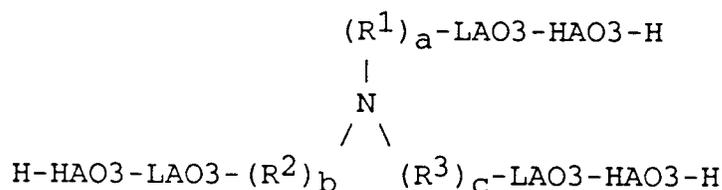LAO3 in each occurrence represents a lipophilic alkylene oxide block unit,

L represents a linking group, such as amine or diamine,

z is 2 and

z' is 1 or 2.

The linking group L can take any convenient form. It is generally preferred to choose a linking group that is itself lipophilic. When z + z' equal three, the linking group must be trivalent. Amines can be used as trivalent linking groups. When an amine is used to form the linking unit L, the polyalkylene oxide block copolymer surfactants employed can take the form shown in formula VII:
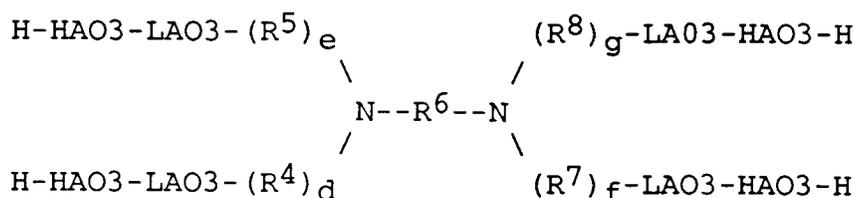
(VII)

$$\begin{array}{c}(R^1)_a\text{-LAO3-HAO3-H}\\ |\\ N\\ /\quad \backslash\\ \text{H-HAO3-LAO3-}(R^2)_b\qquad (R^3)_c\text{-LAO3-HAO3-H}\end{array}$$

where

HAO3 and LAO3 are as previously defined;

R^1, R^2 and R^3 are independently selected hydrocarbon linking groups, preferably phenylene groups or alkylene groups containing from 1 to 10 carbon atoms; and

a, b and c are independently zero or 1. To avoid steric hindrances it is generally preferred that at least one (optimally at least two) of a, b and c be 1. An amine (preferably a secondary or tertiary amine) having hydroxy functional groups for entering into an oxyalkylation reaction is a contemplated starting material for forming a polyalkylene oxide block copolymer satisfying formula VII.

When z + z' equal four, the linking group must be tetravalent. Diamines are preferred tetravalent linking groups. When a diamine is used to form the linking unit L, the polyalkylene oxide block copolymer surfactants employed can take the form shown in formula VIII:

(VIII)

$$\begin{array}{c}\text{H-HAO3-LAO3-}(R^5)_e\qquad\qquad (R^8)_g\text{-LAO3-HAO3-H}\\ \backslash\qquad\qquad /\\ N\text{--}R^6\text{--}N\\ /\qquad\qquad \backslash\\ \text{H-HAO3-LAO3-}(R^4)_d\qquad\qquad (R^7)_f\text{-LAO3-HAO3-H}\end{array}$$

where

HAO3 and LAO3 are as previously defined;

R^4, R^5, R^6, R^7 and R^8 are independently selected hydrocarbon linking groups, preferably phenylene groups or alkylene groups containing from 1 to 10 carbon atoms; and

d, e, f and g are independently zero or 1. It is generally preferred that LAO3 be chosen so that the LOL lipophilic block unit accounts for from 4 to less than 96 percent, preferably from 15 to 95 percent, optimally 20 to 90 percent, of the molecular weight of the copolymer.

In a fourth category, hereinafter referred to as category S-IV surfactants, the polyalkylene oxide block copolymer surfactants employed contain at least three terminal lipophilic alkylene oxide block units linked through a hydrophilic alkylene oxide block linking unit and can be, in a simple form, schematically represented as indicated by formula IX below:

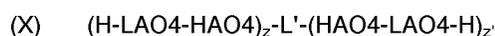(IX) $(H\text{-LAO4})_z\text{-HOL-}(LAO4\text{-H})_{z'}$
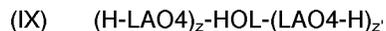
where

LAO4 in each occurrence represents a terminal lipophilic alkylene oxide block unit,

HOL represents a hydrophilic alkylene oxide block linking unit,

z is 2 and

z' is 1 or 2.

The polyalkylene oxide block copolymer surfactants employed can take the form shown in formula X:

(X) $(H\text{-LAO4-HAO4})_z\text{-L'-}(HAO4\text{-LAO4-H})_{z'}$
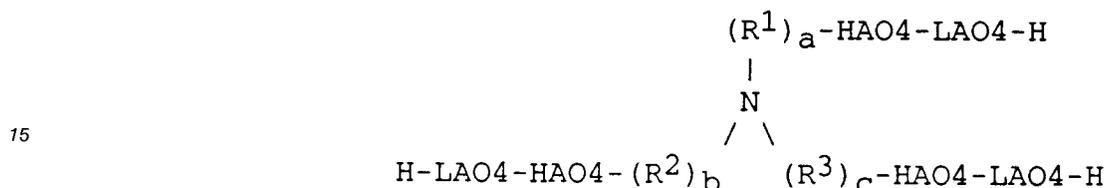
where

HAO4 in each occurrence represents a hydrophilic alkylene oxide block unit,

LAO4 in each occurrence represents a terminal lipophilic alkylene oxide block unit,

L' represents a linking group, such as amine or diamine,

z is 2 and

z' is 1 or 2.

The linking group L' can take any convenient form. It is generally preferred to choose a linking group that is itself hydrophilic. When z + z' equal three, the linking group must be trivalent. Amines can be used as trivalent linking groups. When an amine is used to form the linking unit L', the polyalkylene oxide block copolymer surfactants employed can take the form shown in formula XI:
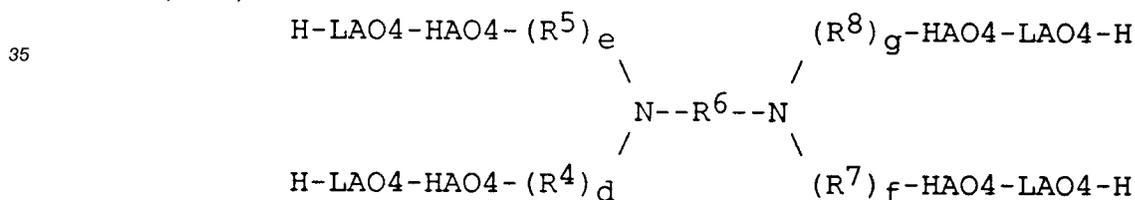
(XI)

```
              (R¹)ₐ-HAO4-LAO4-H
                 |
                 N
               /   \
H-LAO4-HAO4-(R²)_b     (R³)_c-HAO4-LAO4-H
```

where

HAO4 and LAO4 are as previously defined;

R^1, R^2 and R^3 are independently selected hydrocarbon linking groups, preferably phenylene groups or alkylene groups containing from 1 to 10 carbon atoms; and

a, b and c are independently zero or 1.

To avoid steric hindrances it is generally preferred that at least one (optimally at least two) of a, b and c be 1. An amine (preferably a secondary or tertiary amine) having hydroxy functional groups for entering into an oxyalkylation reaction is a contemplated starting material for forming a polyalkylene oxide block copolymer satisfying formula XI.

When z + z' equal four, the linking group must be tetravalent. Diamines are preferred tetravalent linking groups. When a diamine is used to form the linking unit L', the polyalkylene oxide block copolymer surfactants employed can take the form shown in formula XII:
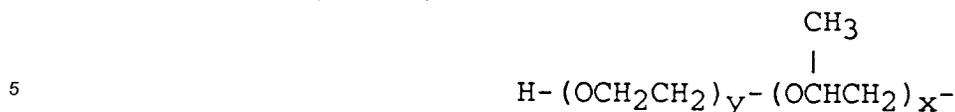
(XII)

```
H-LAO4-HAO4-(R⁵)_e                (R⁸)_g-HAO4-LAO4-H
                   \            /
                    N--R⁶--N
                   /            \
H-LAO4-HAO4-(R⁴)_d                (R⁷)_f-HAO4-LAO4-H
```

where

HAO4 and LAO4 are as previously defined;

R^4, R^5, R^6, R^7 and R^8 are independently selected hydrocarbon linking groups, preferably phenylene groups or alkylene groups containing from 1 to 10 carbon atoms; and

d, e, f and g are independently zero or 1. It is generally preferred that LAO4 be chosen so that the HOL hydrophilic block unit accounts for from 4 to 96 percent, preferably from 5 to 85 percent, of the molecular weight of the copolymer.
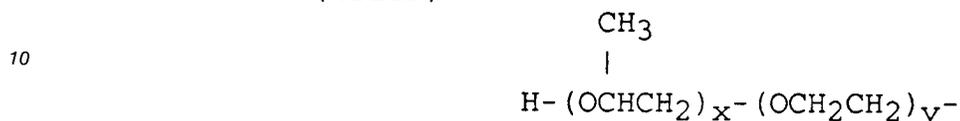
In their simplest possible form the polyalkylene oxide block copolymer surfactants of categories S-III and S-IV employ ethylene oxide repeating units to form the hydrophilic (HAO3 and HAO4) block units and 1,2-propylene oxide repeating units to form the lipophilic (LAO3 and LAO4) block units. At least three propylene oxide repeating units are required to produce a lipophilic block repeating unit. When so formed, each H-HAO3-LAO3- or H-LAO4-HAO4- group satisfies formula XIIIa or XIIIb, respectively:

(XIIIa)

$$H-(OCH_2CH_2)_y-(OCHCH_2)_x-$$
$$\overset{\displaystyle CH_3}{\underset{\displaystyle |}{}}$$

(XIIIb)

$$H-(OCHCH_2)_x-(OCH_2CH_2)_y-$$
$$\overset{\displaystyle CH_3}{\underset{\displaystyle |}{}}$$

where

x is at least 3 and can range up to 250 or more and

y is chosen so that the ethylene oxide block unit maintains the necessary balance of lipophilic and hydrophilic qualities necessary to retain surfactant activity. This allows y to be chosen so that the hydrophilic block units together constitute from greater than 4 to 96 percent (optimally 10 to 80 percent) by weight of the total block copolymer. In this instance the lipophilic alkylene oxide block linking unit, which includes the 1,2-propylene oxide repeating units and the linking moieties, constitutes from 4 to 96 percent (optimally 20 to 90 percent) of the total weight of the block copolymer. Within the above ranges, y can range from 1 (preferably 2) to 340 or more.

The overall molecular weight of the polyalkylene oxide block copolymer surfactants of categories S-III and S-IV have a molecular weight of greater than 1100, preferably at least 2,000. Generally any such block copolymer that retains the dispersion characteristics of a surfactant can be employed. It has been observed that the surfactants are fully effective either dissolved or physically dispersed in the reaction vessel. The dispersal of the polyalkylene oxide block copolymers is promoted by the vigorous stirring typically employed during the preparation of tabular grain emulsions. In general category S-III surfactants having molecular weights of less than about 60,000, preferably less than about 40,000, are contemplated for use, category S-IV surfactants having molecular weight of less than 50,000, preferably less than about 30,000, are contemplated for use.

While commercial surfactant manufacturers have in the overwhelming majority of products selected 1,2-propylene oxide and ethylene oxide repeating units for forming lipophilic and hydrophilic block units of nonionic block copolymer surfactants on a cost basis, it is recognized that other alkylene oxide repeating units can, if desired, be substituted in any of the category S-I, S-II, S-III and S-IV surfactants, provided the intended lipophilic and hydrophilic properties are retained. For example, the propylene oxide repeating unit is only one of a family of repeating units that can be illustrated by formula XIV

(XIV)

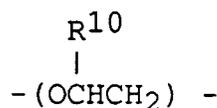$$-(OCHCH_2)-$$
$$\overset{\displaystyle R^9}{\underset{\displaystyle |}{}}$$
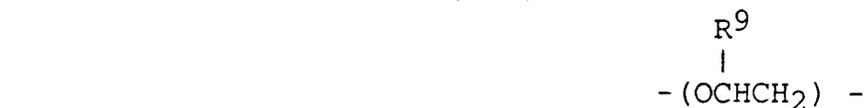
where

R^9 is a lipophilic group, such as a hydrocarbon--e.g., alkyl of from 1 to 10 carbon atoms or aryl of from 6 to 10 carbon atoms, such as phenyl or naphthyl.

In the same manner, the ethylene oxide repeating unit is only one of a family of repeating units that can be illustrated by formula XV:

(XV)

$$-(OCHCH_2) -$$

with R^{10} above the structure.

where

R^{10} is hydrogen or a hydrophilic group, such as a hydrocarbon group of the type forming R^9 above additionally having one or more polar substituents--e.g., one, two, three or more hydroxy and/or carboxy groups.

In each of the surfactant categories each of block units contain a single alkylene oxide repeating unit selected to impart the desired hydrophilic or lipophilic quality to the block unit in which it is contained. Hydrophilic-lipophilic balances (HLB's) of commercially available surfactants are generally available and can be consulted in selecting suitable surfactants.

Only very low levels of surfactant are required in the emulsion at the time parallel twin planes are being introduced in the grain nuclei to reduce the grain dispersity of the emulsion being formed. Surfactant weight concentrations are contemplated as low as 0.1 percent, based on the interim weight of silver--that is, the weight of silver present in the emulsion while twin planes are being introduced in the grain nuclei. A preferred minimum surfactant concentration is 1 percent, based on the interim weight of silver. A broad range of surfactant concentrations have been observed to be effective. No further advantage has been realized for increasing surfactant weight concentrations above 100 percent of the interim weight of silver using category S-I surfactants or above 50 percent of the interim weight of silver using category S-II, S-III or S-IV surfactants. However, surfactant concentrations of 200 percent of the interim weight of silver or more are considered feasible using category S-I surfactants or 100 percent or more using category S-II, S-III or S-IV surfactants.

The preparation process is compatible with either of the two most common techniques for introducing parallel twin planes into grain nuclei. The preferred and most common of these techniques is to form the grain nuclei population that will be ultimately grown into tabular grains while concurrently introducing parallel twin planes in the same precipitation step. In other words, grain nucleation occurs under conditions that are conducive to twinning. The second approach is to form a stable grain nuclei population and then adjust the pAg of the interim emulsion to a level conducive to twinning.

Regardless of which approach is employed, it is advantageous to introduce the twin planes in the grain nuclei at an early stage of precipitation. It is contemplated to obtain a grain nuclei population containing parallel twin planes using less than 2 percent of the total silver used to form the tabular grain emulsion. It is usually convenient to use at least 0.05 percent of the total silver to form the parallel twin plane containing grain nuclei population, although this can be accomplished using even less of the total silver. The longer introduction of parallel twin planes is delayed after forming a stable grain nuclei population the greater is the tendency toward increased grain dispersity.

At the stage of introducing parallel twin planes in the grain nuclei, either during initial formation of the grain nuclei or immediately thereafter, the lowest attainable levels of grain dispersity in the completed emulsion are achieved by control of the dispersing medium.

The pAg of the dispersing medium is preferably maintained in the range of from 5.4 to 10.3 and, for achieving a COV of less than 10 percent, optimally in the range of from 7.0 to 10.0. At a pAg of greater than 10.3 a tendency toward increased tabular grain ECD and thickness dispersities is observed. Any convenient conventional technique for monitoring and regulating pAg can be employed.

Reductions in grain dispersities have also been observed as a function of the pH of the dispersing medium. Both the incidence of nontabular grains and the thickness dispersities of the nontabular grain population have been observed to decrease when the pH of the dispersing medium is less than 6.0 at the time parallel twin planes are being introduced into the grain nuclei. The pH of the dispersing medium can be regulated in any convenient conventional manner. A strong mineral acid, such as nitric acid, can be used for this purpose.

Grain nucleation and growth occurs in a dispersing medium comprised of water, dissolved salts and a conventional peptizer. Hydrophilic colloid peptizers such as gelatin and gelatin derivatives are specifically contemplated. Peptizer concentrations of from 20 to 800 (optimally 40 to 600) grams per mole of silver introduced during the nucleation step have been observed to produce emulsions of the lowest grain dispersity levels.

The formation of grain nuclei containing parallel twin planes is undertaken at conventional precipitation temperatures for photographic emulsions, with temperatures in the range of from 20 to 80°C being particularly preferred and temperature of from 20 to 60°C being optimum.

Once a population of grain nuclei containing parallel twin planes has been established as described above, the next step is to reduce the dispersity of the grain nuclei population by ripening. The objective of ripening grain nuclei containing parallel twin planes to reduce dispersity is disclosed by both Himmelwright U.S. Patent 4,477,565 and Nottorf U.S. Patent 4,722,886. Ammonia and thioethers in concentrations of from about 0.01 to 0.1 N constitute preferred ripening agent selections.

Instead of introducing a silver halide solvent to induce ripening it is possible to accomplish the ripening step by adjusting pH to a high level--e.g., greater than 9.0. A ripening process of this type is disclosed by Buntaine and Brady U.S. Patent 5,013,641. In this process the post nucleation ripening step is performed by adjusting the pH of the dispersing medium to greater than 9.0 by the use of a base, such as an alkali hydroxide (e.g., lithium, sodium or potassium hydroxide) followed by digestion for a short period (typically 3 to 7 minutes). At the end of the ripening step the emulsion is again returned to the acidic pH ranges conventionally chosen for silver halide precipitation (e.g. less than 6.0) by introducing a conventional acidifying agent, such as a a mineral acid (e.g., nitric acid).

Some reduction in dispersity will occur no matter how abbreviated the period of ripening. It is preferred to continue ripening until at least about 20 percent of the total silver has been solubilized and redeposited on the remaining grain nuclei. The longer ripening is extended the fewer will be the number of surviving nuclei. This means that progressively less additional silver halide precipitation is required to produce tabular grains of an aim ECD in a subsequent growth step. Looked at another way, extending ripening decreases the size of the emulsion make in terms of total grams of silver precipitated. Optimum ripening will vary as a function of aim emulsion requirements and can be adjusted as desired.

Once nucleation and ripening have been completed, further growth of the emulsions can be undertaken in any conventional manner consistent with achieving desired final mean grain thicknesses and ECDs. The halides introduced during grain growth can be selected independently of the halide selections for nucleation. The tabular grain emulsion can contain grains of either uniform or nonuniform silver halide composition.

Although the preparation procedures described above are capable of preparing emulsions capable of exhibiting a contrast of greater than 2.0 when the coating coverage is chosen to produce a maximum density of 2.0 or higher, it is recognized that the contrast of the emulsions employed can be further increased, if desired, by incorporating one or more conventional contrast increasing agents in the emulsions. For example, a Group VIII metal dopant known to enhance contrast, such as rhodium, ruthenium or iridium, can be introduced during grain formation. The dopant can be added to the reaction vessel prior to the start of precipitation, but is preferably added after the formation of twin planes during grain growth. The metal can be added to the reaction vessel as a simple salt or as a coordination complex, such as a tetracoordination complex or, preferably, a hexacoordination complex. The ligands of the complex as well as the complexed metal ion can form a part of the completed grain. In one preferred form of addition rhodium, ruthenium or iridium can be added in the form of simple salts of halides, preferably chloride and/or bromide. In another preferred form of addition rhodium, ruthenium or iridium can be added in the form an ammonium or alkali metal hexahalorhodate, iridate or ruthenate, where the halides are preferably chloride or bromide. Any amount of dopant up to about 1×10^{-5} Group VIII metal gram atom per silver mole can be employed. Typically a Group VIII metal ion concentration of at least 10^{-9} (preferably at least 10^{-8}) metal gram atom per silver mole is contemplated to produce a significant further increase in contrast. To avoid excessive desensitization of the emulsions it is preferred to limit Group VIII metal ion concentrations to less than 10^{-6} metal gram atom per silver mole. Research Disclosure, Vol. 308, Dec. 1989, Item 308119, Section I, paragraph D, provides a summary of metal dopant teachings. Evans et al U.S. Patent 5,024,931 discloses the effectiveness of a variety of iridium oligomers as dopants.

In optimizing the process of preparation for minimum tabular grain dispersity levels it has been observed that optimizations differ as a function of iodide incorporation in the grains as well as the choices of surfactants and/or peptizers.

While any conventional hydrophilic colloid peptizer can be employed, it is preferred to employ gelatino-peptizers during precipitation. Gelatino-peptizers are commonly divided into so-called "regular" gelatino-peptizers and so-called "oxidized" gelatino-peptizers. Regular gelatino-peptizers are those that contain naturally occurring amounts of methionine of at least 30 micromoles of methionine per gram and usually considerably higher concentrations. The term oxidized gelatino-peptizer refers to gelatino-peptizers that contain less than 30 micromoles of methionine per gram. A regular gelatino-peptizer is converted to an oxidized gelatino-peptizer when treated with a strong oxidizing agent, such as taught by Maskasky U.S.

Patent 4,713,323 and King et al U.S. Patent 4,942,120. The oxidizing agent attacks the divalent sulfur atom of the methionine moiety, converting it to a tetravalent or, preferably, hexavalent form. While methionine concentrations of less than 30 micromoles per gram have been found to provide oxidized gelatino-peptizer performance characteristics, it is preferred to reduce methionine concentrations to less than 12 micromoles per gram. Any efficient oxidation will generally reduce methionine to less than detectable levels. Since gelatin in rare instances naturally contains low levels of methionine, it is recognized that the terms "regular" and "oxidized" are used for convenience of expression while the true distinguishing feature is methionine level rather than whether or not an oxidation step has been performed.

When an oxidized gelatino-peptizer is employed, it is preferred to maintain a pH during twin plane formation of less than 5.2 to achieve a minimum (less than 10 percent) COV. When a regular gelatino-peptizer is employed, the pH during twin plane formation is maintained at less than 3.0 to achieve a minimum COV.

When regular gelatin and a category S-I surfactant are each employed prior to post-ripening grain growth, the category S-I surfactant is selected so that the hydrophilic block (e.g., HAO1) accounts for 4 to 96 (preferably 5 to 85 and optimally 10 to 80) percent of the total surfactant molecular weight. It is preferred that x and x' (in formula II) be at least 6 and that the minimum molecular weight of the surfactant be at least 760 and optimally at least 1000, with maximum molecular weights ranging up to 16,000, but preferably being less than 10,000.

When the category S-I surfactant is replaced by a category S-II surfactant, the latter is selected so that the lipophilic block (e.g., LAO2) accounts for 4 to 96 (preferably 15 to 95 and optimally 20 to 90) percent of the total surfactant molecular weight. It is preferred that x (formula IV) be at least 13 and that the minimum molecular weight of the surfactant be at least 800 and optimally at least 1000, with maximum molecular weights ranging up to 30,000, but preferably being less than 20,000.

When a category S-III surfactant is selected for this step, it is selected so that the lipophilic alkylene oxide block linking unit (LOL) accounts for 4 to 96 percent, preferably 15 to 95 percent, and optimally 20 to 90 percent of the total surfactant molecular weight. In the ethylene oxide and 1,2-propylene oxide forms shown in formula (XIIIa), x can range from 3 to 250 and y can range from 2 to 340 and the minimum molecular weight of the surfactant is greater than 1,100 and optimally at least 2,000, with maximum molecular weights ranging up to 60,000, but preferably being less than 40,000. The concentration levels of surfactant are preferably restricted as iodide levels are increased.

When a category S-IV surfactant is selected for this step, it is selected so that the hydrophilic alkalylene oxide block linking unit (HOL) accounts for 4 to 96 percent, preferably 5 to 85 percent, and optimally 10 to 80 percent of the total surfactant molecular weight. In the ethylene oxide and 1,2-propylene oxide forms shown in formula (XIIIb), x can range from 3 to 250 and y can range from 2 to 340 and the minimum molecular weight of surfactant is greater than 1,100 and optimally at least 2,000, with maximum molecular weights ranging up to 50,000, but preferably being less than 30,000.

When oxidized gelatino-peptizer is employed prior to post-ripening grain growth and no iodide is added during post-ripening grain growth, minimum COV emulsions can be prepared with category S-I surfactants chosen so that the hydrophilic block (e.g., HAO1) accounts for 4 to 35 (optimally 10 to 30) percent of the total surfactant molecular weight. The minimum molecular weight of the surfactant continues to be determined by the minimum values of x and x' (formula II) of 6. In optimized forms x and x' (formula II) are at least 7. Minimum COV emulsions can be prepared with category S-II surfactants chosen so that the lipophilic block (e.g., LAO2) accounts for 40 to 96 (optimally 60 to 90) percent of the total surfactant molecular weight. The minimum molecular weight of the surfactant continues to be determined by the minimum value of x (formula IV) of 13. The same molecular weight ranges for both category S-I and S-II surfactants are applicable as in using regular gelatino-peptizer as described above.

The polyalkylene oxide block copolymer surfactant can, if desired, be removed from the emulsion after it has been fully prepared. Any convenient conventional washing procedure, such as those illustrated by Research Disclosure, Vol. 308, December 1989, Item 308,119, Section II, can be employed. The polyalkylene oxide block copolymer surfactant constitutes a detectable component of the final emulsion when present in concentrations greater than 0.02 percent, based on the total weight of silver.

Apart from the features described above the phototypesetting papers of the invention can be constructed using conventional features, such as those set out in Research Disclosure, Item 308,119, cited above. Referring to Item 308,119, the emulsions can be washed (Section II), chemically sensitized (Section III), spectrally sensitized (Section IV, but excluding paragraphs G and L), protected by the inclusion of one or more antifoggants and sensitizers (Section VI), and hardeners (Section X). The emulsion and other layers of the photographic elements can include coating aids (Section XI), plasticizers and lubricants (Section XII), antistatic layers (Section XIII), and matting agents (Section XVI). Any conventional reflective support, such

as any reflective form of the various constructions described in Section XVII can be employed. Conventional coating and drying procedures can be employed in forming the emulsion and optional additional layers, such as subbing and overcoat layers, can be employed as described in Section XV. Conventional exposure and processing, illustrated by Sections XVIII and XIX, respectively, are contemplated.

Examples

The invention can be better appreciated by reference to the following specific examples. In the emulsions of the examples greater than 97 percent of total grain projected area was in each instance accounted for by tabular grains. Grains having an equivalent circular diameter of less than 0.1 μm were in each instance absent or present in only such negligible amounts as to have no bearing on the numerical grain parameters reported.

Comparative Example 1 (AgBr, Example 9, Saitou et al U.S. Patent 4,797,354)

In a 4-liter reaction vessel was placed an aqueous gelatin solution (composed of 1 liter of water, 7 g of deionized alkali-processed gelatin, 4.5 g of potassium bromide, 1.2 ml of 1 N potassium hydroxide solution and having pBr of 1.42) and while keeping the temperature thereof at 30°C., 25 ml of an aqueous solution of silver nitrate (containing 8.0 g of silver nitrate) and 25 ml of an aqueous solution of potassium bromide (containing 5.8 g of potassium bromide) were simultaneously added thereto over a period of 1 minute at a rate of 25 ml/min. Then, it was added an aqueous gelatin solution (composed of 1950 ml of water, 90 g of deionized alkali-processed gelatin, 15.3 ml of 1 N aqueous potassium hydroxide solution, and 3.6 g of potassium bromide) and the temperature of the mixture was raised to 75°C over a period of 10 minutes. Thereafter, ripening was performed for 50 minutes.

The mixture was then transferred to a 12-liter vessel, into which 200 ml of an aqueous silver nitrate solution (containing 90 g of silver nitrate) was added at a rate of 20 ml/min. Twenty-five seconds after initiating the addition of silver nitrate, 191.6 ml of an aqueous potassium bromide solution (containing 61.2 g of potassium bromide) was added thereto at a rate of 20 ml/min., the additions of both solutions being finished at the same time. Thereafter, the resultant mixture was stirred for 2 minutes, and then 2,000 ml of an aqueous silver nitrate solution (containing 900 g of silver nitrate) and 2,000 ml of a potassium bromide solution (containing 636.9 g of potassium bromide) were simultaneously added to the aforesaid mixture at a rate of 40 ml/min for the first 20 minutes and 60 ml/min for the subsequent 20 minutes. Then, after stirring the mixture for 1 minute, the silver halide emulsion thus obtained was washed and redispersed. The emulsion grains consisted essentially of silver bromide.

The properties of grains of this emulsion were as follows:
Average Grain ECD: 1.20 μm
Average Grain Thickness: 0.162 μm
Average Aspect Ratio: 7.4
Average Tabularity: 45.7
Coefficient of Variation based on Total Grains: 21.3%

The emulsion was optimally sensitized with 70 mg/mole of sodium thiocyanate, 2.4 mg/mole of potassium tetrachloroaurate, 3.2 mg/mole of sodium thiosulfate pentahydrate, 60 mg/mole of Dye A, 3-ethyl-5-[N-(4-sulfobutyl)-4-(1H)pyridylidene]rhodanine, pyridinium salt, heat treated at 65°C for 35 min. To the finished emulsion were added 300 mg/mole of 5-methyl-s-triazole-(2-3-a)-pyrimidine-7-ol.

Example 2 (AgBr, AKT-731)

In a 4-liter reaction vessel was placed an aqueous gelatin solution (composed of 1 liter of water, 2.5 g of oxidized alkali-processed gelatin, 4.0 ml of 4 N nitric acid solution, 1.12 g of sodium bromide and having pAg of 9.39, and 1.57 wt%, based on total silver introduced up to the beginning of post-ripening grain growth stage, of PLURONIC™-31R1, a surfactant satisfying formula II, x = 25, x' = 25, y = 7) and, while keeping the temperature thereof at 45°C., 8.3 ml of an aqueous solution of silver nitrate (containing 2.26 g of silver nitrate) and equal volume of an aqueous solution of sodium bromide (containing 1.44 g of sodium bromide) were simultaneously added thereto over a period of 1 minute at a constant rate. Then, into the mixture was added 14.2 ml of an aqueous sodium bromide solution (containing 1.46 g of sodium bromide) after 1 minute of mixing. Temperature of the mixture was raised to 60 C over a period of 9 minutes. At that time, 65 ml of an aqueous ammoniacal solution (containing 6.7 g of ammonium sulfate and 48 ml of 2.5 N sodium hydroxide solution) was added into the vessel and mixing was conducted for a period of 9 minutes.

Then, 105.5 ml of an aqueous gelatin solution (containing 16.7 g of oxidized alkali-processed gelatin and 22 ml of 4 N nitric acid solution) was added to the mixture over a period of 2 minutes. Thereafter, 25 ml of an aqueous silver nitrate solution (containing 6.8 g of silver nitrate) and equal volume of an aqueous sodium bromide solution (containing 4.4 g of sodium bromide) were added at a constant rate for a period of 10 minutes. Then, 225 ml of an aqueous silver nitrate solution (containing 61.1 g of silver nitrate) and equal volume of an aqueous sodium bromide solution (containing 38.9 g of sodium bromide) were simultaneously added to the aforesaid mixture at constant ramp starting from respective rate of 2.5 ml/min and 2.6 ml/min for the subsequent 30 minutes. Subsequently, 469 ml of an aqueous silver nitrate solution (containing 127.4 g of silver nitrate) and 466 ml of an aqueous sodium bromide solution (containing 80.5 g of sodium bromide) were simultaneously added to the aforesaid mixture at constant rate over a period of 37.5 minutes. The silver halide emulsion thus obtained was washed and redispersed.

This emulsion was sensitized and finished similarly as the emulsion of Example 1. The properties of grains of this emulsion are as follows:

Average Grain ECD: 1.26 μm
Average Grain Thickness: 0.144 μm
Average Aspect Ratio of the Grains: 8.8
Average Tabularity of the Grains: 60.8
Coefficient of Variation base on Total Grains: 6.3%

Comparative Example 3 (AgBr$_{0.99}$I$_{0.01}$ + Rh, AKT-720)

Example 1 was repeated, except that 159 microgram of ammonium hexachlororhodate (III) was introduced over a period of 2.5 min after emulsion was transferred to the 12-liter vessel, and that 1 mole percent of potassium iodide was additionally added to the potassium bromide solution for the subsequent precipitation. The emulsion thus made contained 1 mole% of iodide and 7.23 x 10^{-8} mole of ammonium hexachlororhodate (III) per silver mole.

This emulsion was sensitized and finished similarly as the emulsion of Example 1. The properties of grains of this emulsion are as follows:

Average Grain ECD: 1.30 μm
Average Grain Thickness: 0.148 μm
Average Aspect Ratio of the Grains: 8.8
Average Tabularity of the Grains: 59.3
Coefficient of Variation based on Total Grains: 19.2%

Example 4 (AgBr$_{0.99}$I$_{0.01}$ + Rh, AKT-728)

In a 4-liter reaction vessel was placed an aqueous gelatin solution (composed of 1 liter of water, 1 g of alkali-processed gelatin, 1 ml of 4 N nitric acid solution, 2.44 g of sodium bromide and having pAg of 9.71, and 3.47 wt%, based on total silver introduced up to the beginning of post-ripening grain growth stage, of PLURONIC™-L63, a surfactant satisfying formula IV, x = 32, y = 9, y' = 9) and, while keeping the temperature thereof at 45°C., 6.7 ml of an aqueous solution of silver nitrate (containing 0.91 g of silver nitrate) and equal volume of an aqueous solution of sodium bromide (containing 0.63 g of sodium bromide) were simultaneously added thereto over a period of 1 minute at a constant rate. After 1 minute of mixing, temperature of the mixture was raised to 60°C over a period of 9 minutes. At that time, 28.5 ml of an aqueous ammoniacal solution (containing 1.68 g of ammonium sulfate and 11.8 ml of 2.5 N sodium hydroxide solution) was added into the vessel and mixing was conducted for a period of 9 minutes. Thereafter, 88.7 ml of an aqueous gelatin solution (containing 16.7 g of alkali-processed gelatin and 5.3 ml of 4 N nitric acid solution) was added to the mixture over a period of 2 minutes. 31.6 microgram of ammonium hexachlororhodate (III) was subsequently introduced over a period of 2.5 min. After then, 7.5 ml of an aqueous silver nitrate solution (containing 1.0 g of silver nitrate) and 7.3 ml of an aqueous sodium bromide solution (containing 0.68 g of sodium bromide) were added at a constant rate for a period of 5 minutes. Then, 474.7 ml of an aqueous silver nitrate solution (containing 129 g of silver nitrate) and 473.6 ml of an aqueous halide solution (containing 81 g of sodium bromide and 1.3 g of potassium iodide) were simultaneously added to the aforesaid mixture at constant ramp starting from respective rate of 1.5 ml/min and 1.6 ml/min for the subsequent 64 minutes. Then, 253.3 ml of an aqueous silver nitrate solution (containing 68.9 g of silver nitrate) and 251.1 ml of an aqueous halide solution (containing 43 g of sodium bromide and 0.7 g of potassium iodide) were simultaneously added to the aforesaid mixture at constant rate over a period of 19 minutes. The silver halide emulsion thus obtained contained 1 mole% of iodide and 7.23

15

x 10^{-8} mole of ammonium hexachlororhodate (III) per silver mole.

The properties of grains of this emulsion are as follows:

Average Grain ECD: 1.58 μm

Average Grain Thickness: 0.118 μm

Average Aspect Ratio of the Grains: 13.4

Average Tabularity of the Grains: 113.5

Coefficient of Variation based on Total Grains: 10.4%

Example 5 (AgBr$_{0.99}$I$_{0.01}$ + Rh, AKT-730)

Example 4 was repeated, except that the amount of PLURONIC™-L63 added was increased to 5.21 wt%. The silver halide emulsion thus obtained contained 1 mole% of iodide and 7.23 x 10^{-8} mole of ammonium hexachlororhodate (III) per silver mole.

The emulsion were sensitized and finished similarly as the emulsion of Example 1. The properties of grains of this emulsion are as follows:

Average Grain ECD: 1.35 μm

Average Grain Thickness: 0.153 μm

Average Aspect Ratio of the Grains: 8.8

Average Tabularity of the Grains: 57.7

Coefficient of Variation based on Total Grains: 7.0%

Example 6 (AgBr$_{0.99}$I$_{0.01}$ + Rh, AKT-729)

Example 4 was repeated, except that the amount of PLURONIC™-L63 added was increased to 6.94 wt%. The silver halide emulsion thus obtained contained 1 mole% of iodide and 7.23 x 10^{-8} mole of ammonium hexachlororhodate (III) per silver mole.

The properties of grains of this emulsion are as follows:

Average Grain ECD: 1.22 μm

Average Grain Thickness: 0.186 μm

Average Aspect Ratio of the Grains: 6.6

Average Tabularity of the Grains: 35.3

Coefficient of Variation of Total Grains: 6.3%

Example 7 (AgBr$_{0.99}$I$_{0.01}$ + Ir, AKT-761)

Example 5 was repeated, except that 0.235 mg of potassium hexachloroiridate (IV) was added in place of ammonium hexachlororhodate (III). The silver halide emulsion thus obtained contained 1 mole% of iodide and 4.3 x 10^{-7} mole of potassium hexachloroiridate (IV) per silver mole.

The properties of grains of this emulsion are as follows:

Average Grain ECD: 1.33 μm

Average Grain Thickness: 0.159 μm

Average Aspect Ratio of the Grains: 8.4

Average Tabularity of the Grains: 52.6

Coefficient of Variation based on Total Grains: 7.7%

Coatings and Processing

The emulsion of Comparative Example 1 was compared with the emulsion of Example 2 to provide a silver bromide comparison. The emulsion of Comparative Example 3 was compared with the emulsion of Example 5 to provide a silver bromoiodide comparison. The Example 5 emulsion was selected for comparison with the emulsion of Comparative Example 3 based on their similarities in average grain ECD, thickness and aspect ratio.

The emulsion comparisons are based on identical silver coverages, corresponding to silver coverages of 21.52 mg/dm^2 (200 mg/ft^2) on transparent film support (chosen to permit accurate measurements of maximum density) and 10.76 mg/dm^2 (100 mg/ft^2) on white reflective paper support. The coatings were each processed in Developer A described in Table XV for 1 min at 35°C and in Fixer A described in Table XVI for 30 sec.

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Table XV

Composition of Developer A	
	gram
Water	539.0
Potassium hydroxide, 45.5% solution	178.0
Sodium metabisulfite	145.0
Sodium bromide	12.0
2-butene-dioic acid (z), homopolymer, 50 % solution	13.0
Pentetic acid, pentasodium salt, 40% solution	15.0
Sodium hydroxide, 50% solution	56.0
Benzotriazole	0.4
1-Phenyl-5-mercaptotetrazole	0.05
Boric acid	6.94
Diethylene glycol	110.0
Hydroquinone	75.0
4-Hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidone	2.9
Potassium carbonate, 47% solution	120.0

Table XVI

Composition of Fixer A	
	gram/liter
Ammonia thiosulfate	155.0
Sodium metabisulfite	190.0
Sodium acetate/acetic acid	25.0
Sodium borate, 5-hydrate	11.8
Aluminum sulfate	6.6

The photographic responses for Comparative Example 1 and Example 2 coatings with 1/10 sec exposure to 3000°K light temperature are shown in Fig. 4 and summarized in Table XVII. The superior photographic performance demonstrated by the invention emulsion, Emulsion 2, over Comparative Emulsion 1 is clear in not only contrast but also in speed with matching fog.

In each of Tables XVII, XVIII, and XIX speed was measured at a density of 1.0 above fog. Contrast was measured as the slope of the characteristic curve between a first point lying at a density of 0.2 above fog to a second point on the characteristic curve representing a 0.75 logE higher exposure than the first point.

Table XVII

Emulsion	Fog	Speed	Contrast
1 (Comparison)	0.04	153	1.13
2 (Invention)	0.04	213	1.46

Comparative Emulsion 3 and Emulsion 5 are compared in Figure 5. The superior photographic performance demonstrated by the invention emulsion, Emulsion 5, over Emulsion 3 is again clear in not only contrast but also in speed and fog. It is especially noticeable in the sharper shoulder contrast shown by Emulsion 5. The results are summarized in Table XVIII.

Table XVIII

Emulsion	Fog	Speed	Contrast
3 (Comparison)	0.06	221	1.37
5 (Invention)	0.05	233	1.70

Since high intensity, short time exposure is commonly used in graphic arts products, the optimally sensitized Comparative Emulsion 3 and Example 5 were further evaluated under this condition. The results of coatings subject to 10^{-5} sec exposure are shown in Fig. 6 and summarized in Table XIX. The superiority of Emulsion 5 over Comparative Emulsion 3 is maintained under the higher intensity conditions of exposure.

Table XIX

Emulsion	Fog	Speed	Contrast
3 (Comparison)	0.03	145	1.80
5 (Invention)	0.03	160	1.94

Claims

1. A phototypesetting paper comprised of
   a white reflective support and
   an imaging layer unit coated on the support exhibiting a maximum density of at least 2.0 and a contrast in excess of 2.0 over a 0.75 log E exposure range measured from the minimum exposure required to produce a density of 0.2 above fog,
   the imaging layer unit being comprised of a tabular grain silver halide emulsion having a grain halide content of from 0 to 5 mole percent chloride, from 0 to 15 mole percent iodide and from 80 to 100 mole percent bromide, based on total silver,
   CHARACTERIZED IN THAT
   the coefficient of variation of the tabular grain emulsion is less than 15 percent, based on the total grain population of the emulsion having an equivalent circular diameter of greater than 0.1 μm, and
   greater than 97% of the projected area of the total grain population of said emulsion having an equivalent circular diameter of greater than 0.1 μm is accounted for by tabular grains having a mean thickness of less than 0.2 μm and a tabularity of greater than 25.

2. A phototypesetting paper according to claim 1 further characterized in that the tabular grains have a mean equivalent circular diameter in the range of from 0.4 to 10 μm.

3. A phototypesetting paper according to claim 2 further characterized in that the tabular grains have a mean equivalent circular diameter of less than 5 μm.

4. A phototypesetting paper according to any one of claims 1 to 3 inclusive further characterized in that the tabular grains have an average aspect ratio of up to 100.

5. A phototypesetting paper according to claim 4 further characterized in that the tabular grains have an average aspect ratio in the range of from 10 to 60.

6. A phototypesetting paper according to any one of claims 1 to 5 inclusive further characterized in that the tabular grains are comprised of at least 90 mole percent bromide, based on total silver.

7. A phototypesetting paper according to claim 6 further characterized in that the tabular grains are silver bromide grains.

8. A phototypesetting paper according to any one of claims 1 to 6 inclusive further characterized in that the tabular grains are silver bromoiodide grains.

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9. A phototypesetting paper according to claim 8 further characterized in that the tabular grains contain less than 5 mole percent iodide.

10. A phototypesetting paper according to any one of claims 1 to 9 inclusive further characterized in that the tabular grains contain a contrast enhancing dopant.

11. A phototypesetting paper according to claim 10 further characterized in that the tabular grains contain at least one of rhodium, iridium and ruthenium in an amount sufficient to increase contrast.

12. A phototypesetting paper according to any one of claims 1 to 11 inclusive further characterized in that at least one polyalkylene oxide block copolymer capable of reducing tabular grain dispersity is present.

13. A phototypesetting paper according to claim 12 further characterized in that the polyalkylene oxide block copolymer is selected to satisfy one of the formulae

(S-I)   LAO1-HAO1-LAO1,

(S-II)   HAO2-LAO2-HAO2,

(S-III) $(H\text{-}HAO3)_z\text{-}LOL\text{-}(HAO3\text{-}H)_{z'}$,

and

(S-IV) $(H\text{-}LAO4)_z\text{-}HOL\text{-}(LAO4\text{-}H)_{z'}$

where
LAO1 and LAO4 in each occurrence represents a terminal lipophilic alkylene oxide block unit,
HAO2 and HAO3 in each occurrence presents a terminal hydrophilic alkylene oxide block unit,
HAO1 and HOL each represents a hydrophilic alkylene oxide block linking unit,
LAO2 and LOL each represents a lipophilic alkylene oxide block linking unit,
z is 2, and
z' is 1 or 2,
each block linking unit constitutes from 4 to 96 percent of the block copolymer on a weight basis,
the block copolymer S-I has a molecular weight of from 760 to less than 16,000,
the block copolymer S-II has a molecular weight of from 1,000 to 30,000,
the block copolymer S-III has a molecular weight of from 1,100 to 60,000, and
the block copolymer S-IV has a molecular weight of from 1,100 to 50,000.

14. A phototypesetting paper according to claim 13 further characterized in that
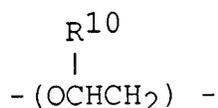(a) each lipophilic alkylene oxide block contains repeating units satisfying the formula:

$$-(OCHCH_2)- \\ \overset{\displaystyle R^9}{\overset{|}{}}$$
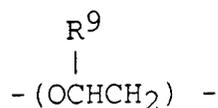
where
R^9 is a hydrocarbon containing from 1 to 10 carbon atoms, and
(b) each hydrophilic alkylene oxide block contains repeating units satisfying the formula:

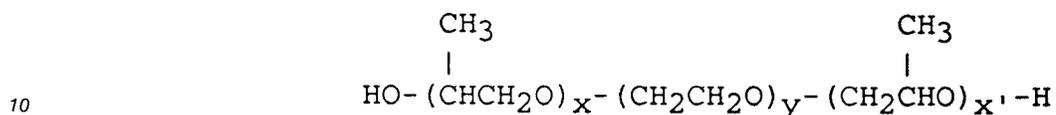$$-(OCHCH_2)- \\ \overset{\displaystyle R^{10}}{\overset{|}{}}$$

where

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R^{10} is hydrogen or a hydrocarbon containing from 1 to 10 carbon atoms substituted with at least one polar substituent.
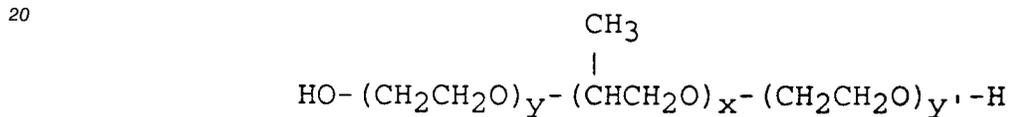
15. A phototypesetting paper according to claim 13 further characterized in that the polyalkylene oxide block copolymer satisfies the formula:

$$HO-(\overset{\overset{\displaystyle CH_3}{\overset{\displaystyle |}{}}}{C}HCH_2O)_x-(CH_2CH_2O)_y-(CH_2\overset{\overset{\displaystyle CH_3}{\overset{\displaystyle |}{}}}{C}HO)_{x'}-H$$

where
    x and x' are each in the range of from 6 to 120 and
    y is in the range of from 2 to 300.

16. A phototypesetting paper according to claim 13 in which the polyalkylene oxide block copolymer satisfies the formula:

$$HO-(CH_2CH_2O)_y-(\overset{\overset{\displaystyle CH_3}{\overset{\displaystyle |}{}}}{C}HCH_2O)_x-(CH_2CH_2O)_{y'}-H$$

where
    x is in the range of from 13 to 490 and
    y and y' are in the range of from 1 to 320.

17. A phototypesetting paper according to any one of claims 1 to 16 inclusive further characterized in that the coefficient of variation of the tabular grain emulsion is less than 10 percent, based on the total grain population having an equivalent circular diameter of greater than 0.1 μm.
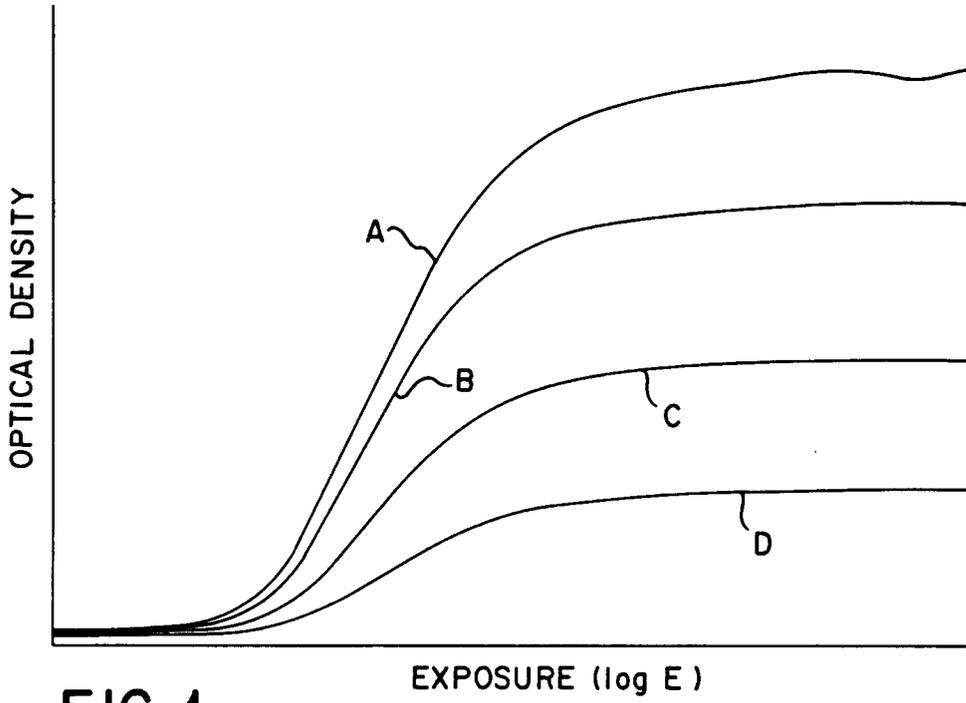
FIG. 1

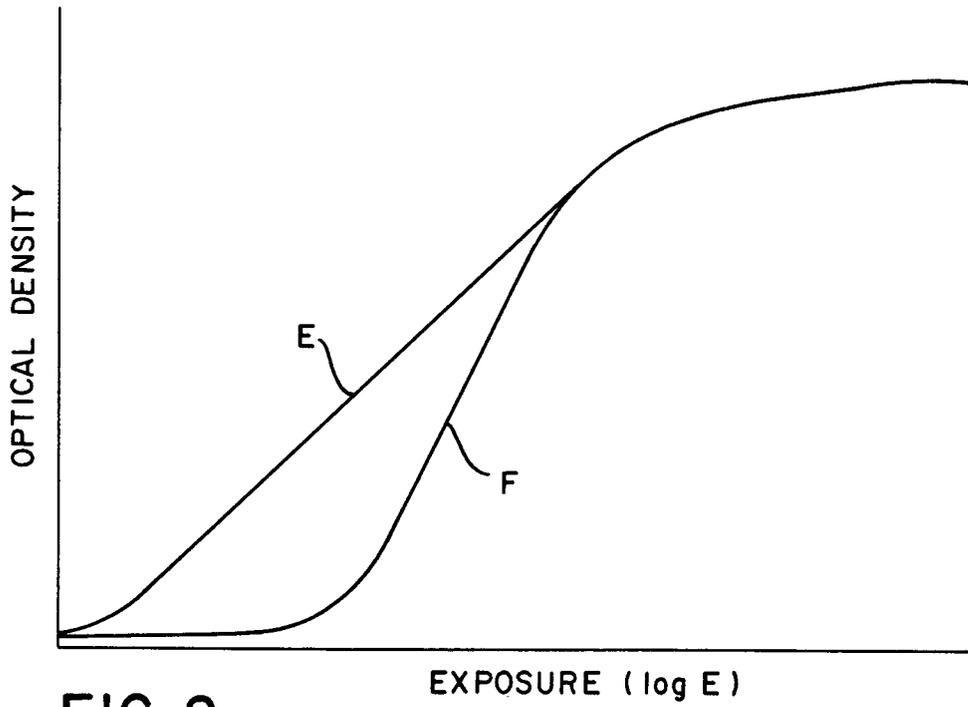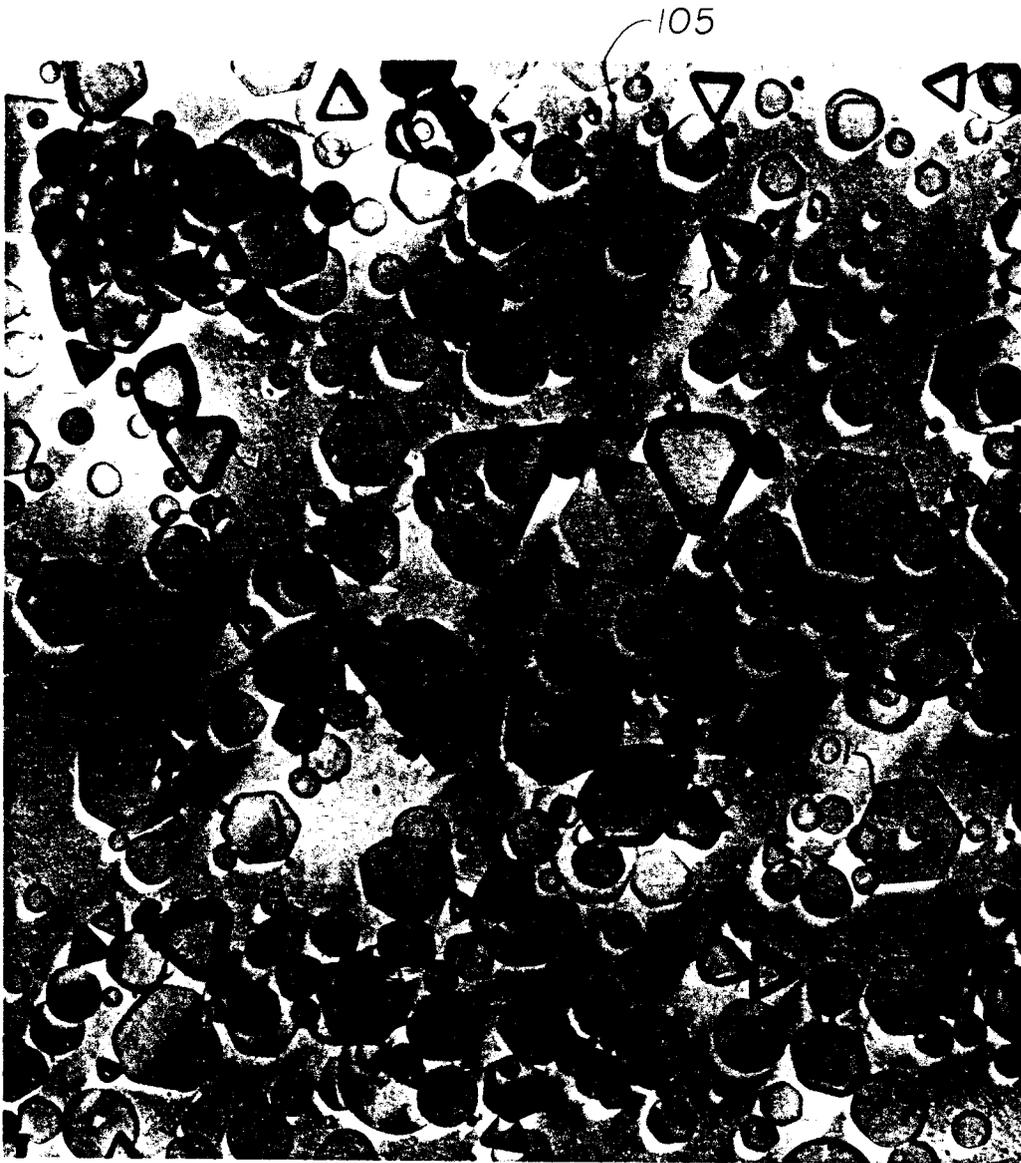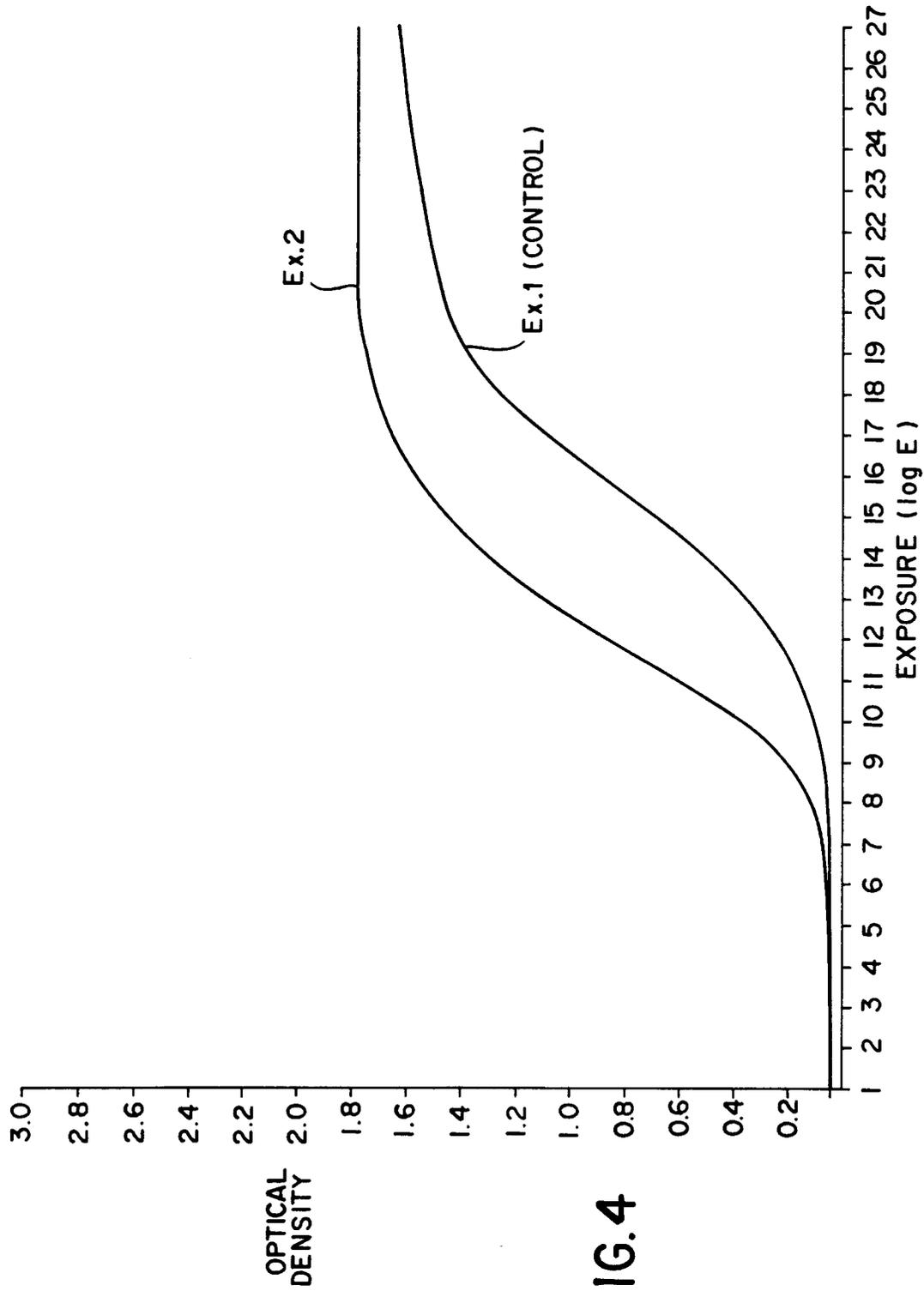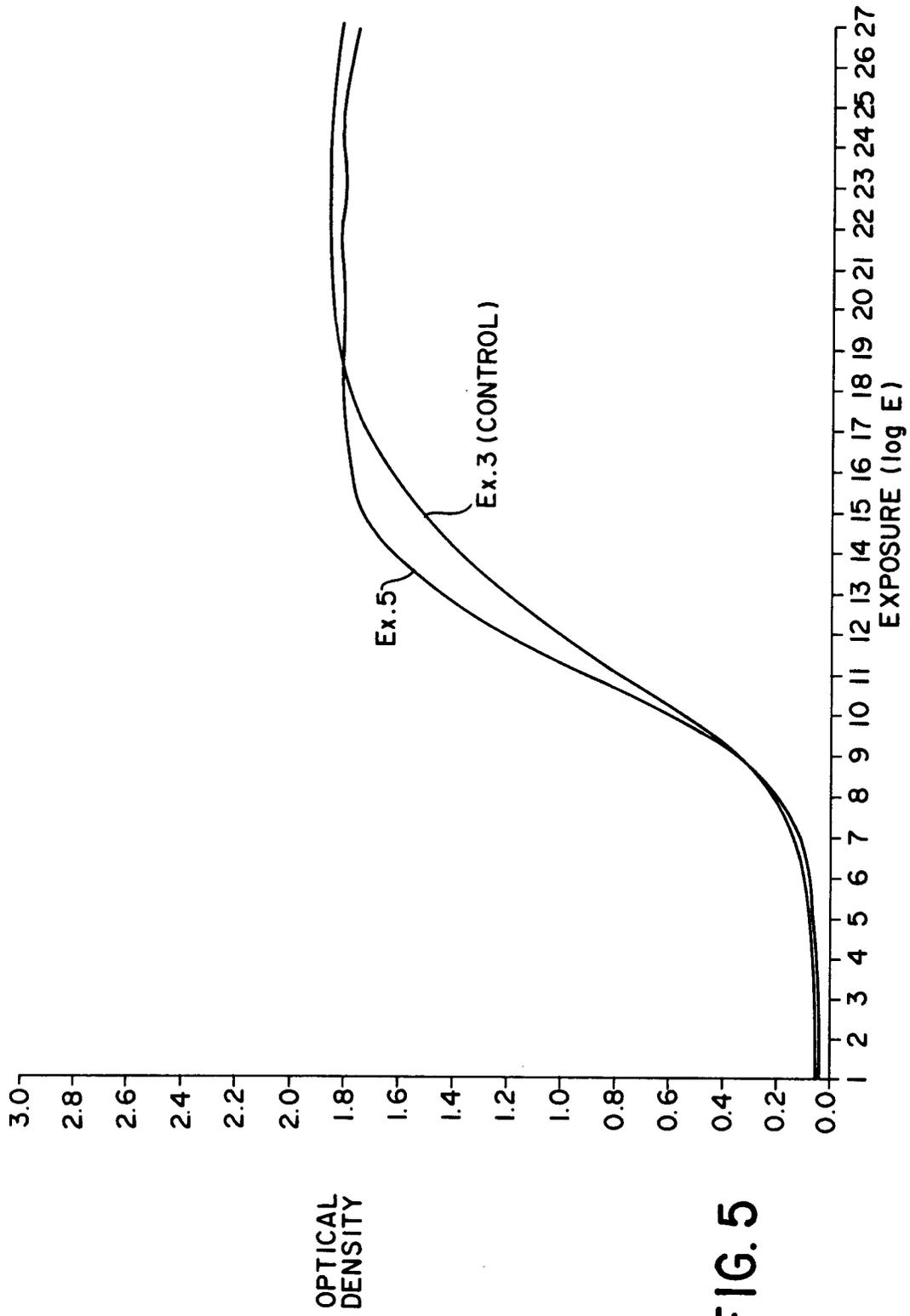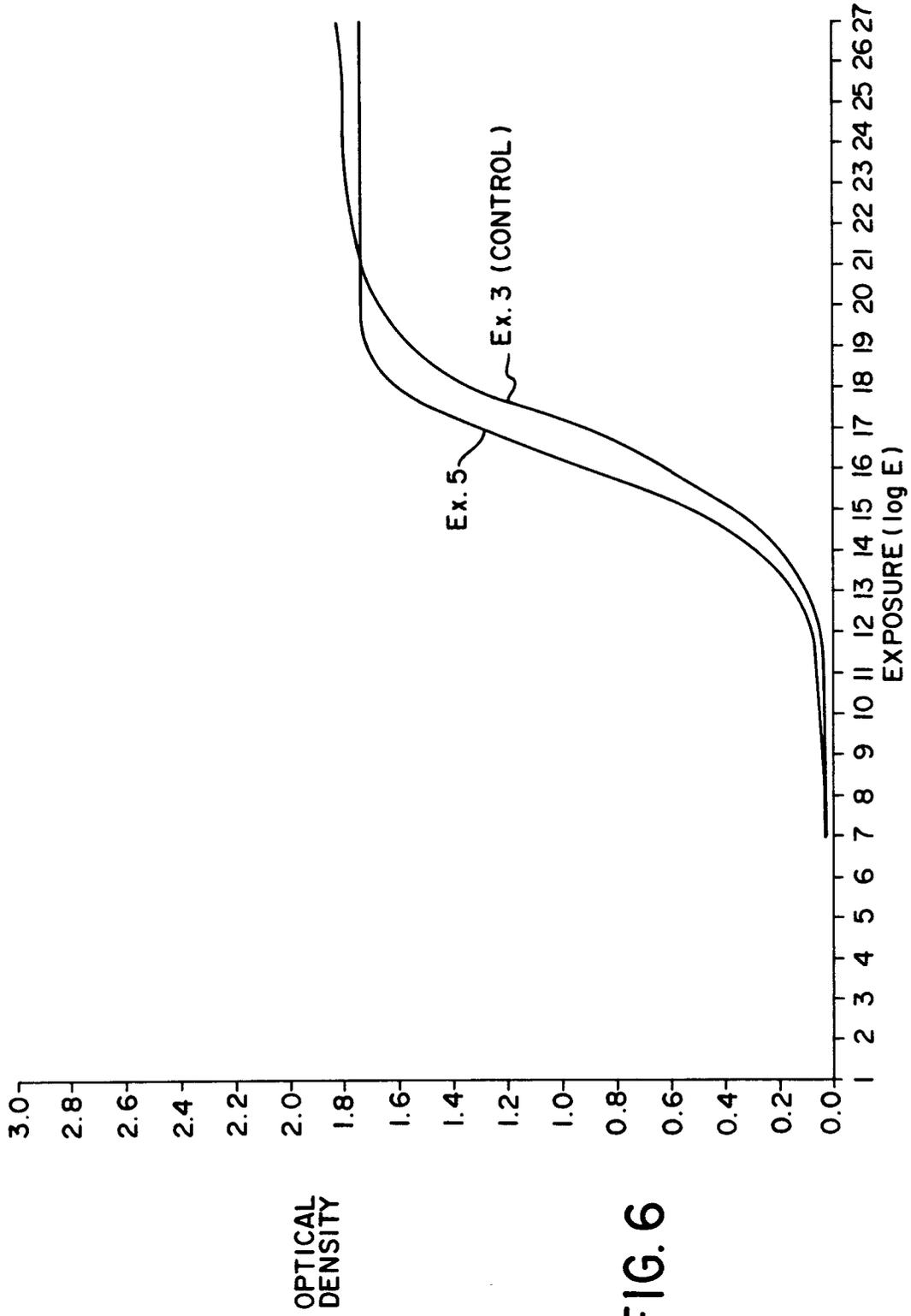

FIG. 2

FIG. 3
(PRIOR ART)

FIG.4

FIG. 5

FIG.6

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)
D,X Y	US-A-4 797 354 (M.SAITOU ET AL.) * column 14, line 3-6; claim 5; example 9 * ---	1-11 12-16	G03C1/035 G03C1/775 G03C1/07
Y	GB-A-808 228 (ILFORD LIMITED) * column 11, line 24 - line 27; table 2 * ---	12-16	
D,A	JOURNAL OF THE AMERICAN OIL CHEMISTS' SOCIETY. vol. 54, no. 3, 1977, CHAMPAIGN US I.R.SCHMOLKA: 'A Review of Block Copolymer Surfactants' * "Introduction" and "Application Areas" * -----	12-16	

	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	09 SEPTEMBER 1992	BUSCHA A.J.

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