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(54) Title: IMAGING ELEMENTS CONTAINING PIGMENTED LAYERS

(57) Abstract

An element containing a pigmented layer comprising a film-forming binder, a pigment and an organophosphonic acid or salt which is a dispersing aid for the pigment. The pigmented layer is located between the support for the element and an image-forming or image-receiving layer.
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IMAGING ELEMENTS CONTAINING PIGMENTED LAYERS

This invention relates to image-forming and image-receiving elements containing layers coated from pigmented compositions comprising organo-polysosphonic acids or salts. Such acids or salts function as dispersing aids for the pigments.

It is known to use a dispersing aid in a pigmented coating composition to more uniformly disperse the pigment in the composition. Such a dispersing aid is conventionally used in forming a pigmented layer of an image-forming or image-receiving element, for example, a photographic element. Such a pigmented layer is often employed in an "underlayer" which is located between the support for the element and the image-forming or image-receiving layer to provide whiteness and increased image sharpness. For example, as described in Research Disclosure, publication 15162, November 1976, page 82, column 2, dispersing aids are used for dispersing white inorganic pigments such as titanium dioxide in light reflecting underlayers in color diffusion transfer elements. As disclosed in that Research Disclosure publication, sodium polymethacrylate is a preferred dispersant for this purpose. Unfortunately, as illustrated in the following Example, the presence of an anionic dispersant such as sodium polymethacrylate in a pigmented underlayer can detrimentally affect the hardness of an image-forming or image-receiving element containing the pigmented layer. This is, of course, a serious disadvantage in the art of image formation.

The problem of this invention is to provide an image-forming or image-receiving element having a pigmented underlayer that contains a dispersing aid which does not detrimentally affect the hardness of
an image-forming or image-receiving element containing such layer. The solution to this problem is the use of an organopolyphosphonic acid or salt as the dispersing aid in a pigmented layer of the type described hereinbefore. Thus, this invention provides an element that comprises a support having thereon a layer that (a) comprises a film-forming binder, a pigment and a dispersing aid for the pigment and, (b) is located between the support on an image-forming or image-receiving layer, and is characterized in that the dispersing aid is an organopolyphosphonic acid or salt.

A significant feature of this invention is that the use of an organopolyphosphonic acid or salt in the pigmented coating composition provides a composition that can be readily formulated without pigment agglomeration and severe settling. The composition can be stored with the pigments remaining adequately dispersed over a lengthy period of time. Because of this stability, plugging of filtration and coating equipment is substantially reduced. The resulting coating has fewer pigment agglomerations and the image-forming or image-receiving elements containing such pigments are less likely to exhibit poor layer adhesion and cracking. Eliminating or substantially reducing such defects as poor layer adhesion and cracking are very important in the art of image formation.

The film-forming binder useful in the practice of this invention can be any binder which can be applied to a substrate (e.g. a resin-coated paper substrate) to provide a uniform coating. Useful binders are well known by workers skilled in the photographic coating art. Examples of useful binders are described, for example, in Research Disclosure, publication 17643, paragraph IX.
(published December, 1978 by Industrial Opportunities, Ltd., Homewell, Havant Hampshire PO9 1EF, United Kingdom), and include both natural and synthetic, colloidal and resin materials. A mixture of binders can be used, if so desired. Preferably, the binder is a hydrophilic colloid or resin, including starches, vinyl pyrrolidone polymers, poly(vinyl alcohol), cellulose ethers and gelatin (which can be acid- or alkali-processed). The binder can also be provided from radiation-curable oligomers or precursors, such as polyacrylated oligomeric compositions which can be polymerized with suitable irradiation (e.g. a beam of electrons or ultraviolet light). The binders useful in the practice of this invention are either readily available from commercial sources or readily prepared by techniques known in the art. The film-forming binders can be mixed with materials which are not film-forming alone, but which also act as binders, as long as the overall film-forming property of the composition is not significantly diminished.

The pigment useful in the practice of this invention includes any of the pigments typically used in image-forming or image-receiving elements of the type described. Such pigments provide a desired coloration and/or reflection of incident radiation. Although the size of the pigment particles can vary widely, the average particle size is generally from 0.4 to 2000 micrometers. Preferably, the pigment is an inorganic pigment, often an inorganic pigment which provides a high degree of reflection of incident radiation, such as a white inorganic pigment. Examples of useful inorganic pigments include zinc oxide, barium sulfate, talc, clays of
various kinds, lead carbonate, antimony oxide, zinc sulfide, zinc phosphate, titanium dioxide (rutile or anatase), calcium metasilicate, trihydrated alumina and calcium carbonate. Titanium dioxide (with or without surface treatment) is preferred. Mixtures of pigments can be used if so desired.

The pigmented layers present in the elements of this invention include one or more organopolyphosphonic acid or salt dispersing aids which keep the pigment uniformly dispersed during formulation of the coating composition and subsequent coating of the composition. The organopolyphosphonic acids, salts or mixtures that are used are hydrolytically and thermally stable.

Examples of useful materials include phosphated ethoxylates or alcohols, which are phosphate coesters derived from combinations of ethoxylates or alcohols respectively.

Typical dispersing aids useful in this invention have at least two \(-\text{P}(\text{OX})_2\) (phosphonic) groups which are defined hereinafter. Other useful organopolyphosphonic acids and salts can be represented by the formula (I):

\[
\begin{align*}
R^2 & \quad \text{O} \\
R^1 & \quad \text{C} \quad \text{P(OX)}_2 \\
R^3 &
\end{align*}
\]

wherein \(X\) is a monovalent cation, such as hydrogen, an alkali metal ion (e.g. sodium or potassium ion), ammonium ion or a quaternary amino ion. Preferably, \(X\) is hydrogen or an alkali metal ion. \(R^1\) is
substituted or unsubstituted alkyl, preferably of 1 to 6 carbon atoms, e.g. methyl, chloromethyl, 2-hydroxyethyl or t-butyl, or

\[
\begin{align*}
R^4 & \quad N^- \quad R^1 \\
R^5 & \quad \text{preferably containing at least one}
\end{align*}
\]

- \( P(OX)_2 \) group; and \( R^2 \) and \( R^3 \) are independently hydrogen, hydroxy, substituted or unsubstituted alkyl, preferably of 1 to 6 carbon atoms, or \(- P(OX)_2 \), provided that if each of \( R^2 \) and \( R^3 \) is hydrogen, hydroxy or alkyl, \( R^1 \) is

\[
\begin{align*}
R^4 & \quad N^- \quad \text{containing at least one} \\
R^5 & \quad \text{\(- P(OX)_2 \) group. In}
\end{align*}
\]

the amino moiety \( R^4 \), \( R^4 \) is hydrogen, an aliphatic group, preferably of from 1 to 30 carbon atoms, or

\[
\begin{align*}
R^2 & \quad \text{-} \quad P(OX)_2 \quad \text{wherein} \\
R^3 & \quad X, \quad R^2 \quad \text{and} \quad R^3 \quad \text{are as defined}
\end{align*}
\]

hereinbefore. \( R^5 \) is hydrogen, an aliphatic group, preferably of from 1 to 30 carbon atoms, or

\[
\begin{align*}
R^2 & \quad \text{-} \quad P(OX)_2 \quad \text{wherein} \\
R^3 & \quad X, \quad R^2 \quad \text{and} \quad R^3 \quad \text{are as defined}
\end{align*}
\]

hereinbefore. \( R^5 \) is hydrogen, an aliphatic group, preferably of from 1 to 30 carbon atoms,
\[
\begin{align*}
R^2 & \quad O \\
C \quad & \quad P(OX)_2, \text{ or } \quad R^2 & \quad Z \\
\quad & \quad \quad R^3 \\
\quad & \quad N \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad 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has from 1 to 6 carbon atoms. Examples of aliphatic groups include alkyl, alkyne-oxy-alkyl, alkyne-thio-alkyl and alkyne-oxy-alkylene-oxy-alkyl.

Preferred dispersing aids useful in practicing this invention are organoaminopoly-phosphonic acids or salts thereof. Suitable compounds can be represented by the foregoing formula (I) wherein

\[ R^1 \text{ is the amino group } \]
\[ R^2 \text{ and } R^3 \text{ are independently hydrogen, } \]
\[ \text{hydroxy or alkyl, and } R^4 \text{ and } R^5 \text{ are as defined hereinabove, provided that either } \]
\[ R^4 \text{ or } R^5 \text{ contains at least 1 } \]
\[ \text{and preferably the amino group } \]
\[ \text{contains at least two } -P(\text{OX})_2 \text{ groups, and } \]
\[ \text{more preferably, it contains three or more of such groups.} \]

More preferably in the foregoing formula (I) in

\[ R^1 \text{, } R^4 \text{ is } -C=\overset{\text{O}}{\overset{\text{Z}^1}{N}} \text{, and } R^5 \text{ is } \]
\[ (\overset{\text{O}}{\overset{\text{Z}^1}{N}}) \text{ where } m \text{ is an integer of from 1 to 10, each of } Z \]
\[ \text{and } Z^1 \text{ is } -C=\overset{\text{O}}{\overset{\text{Z}^1}{N}} \text{, } R^2 \text{ and } R^3 \text{ are independently } \]
hydrogen or alkyl of 1 to 3 carbon atoms; and X is hydrogen or an alkali metal cation, most preferably, sodium. Examples of compounds wherein the scope of the foregoing formula (I) include:

1. Ethylene diamine tetra(methylene phosphonic acid) and salts thereof

\[ (\text{OX})_2\text{OPCH}_2 \quad \text{N} - \text{CH}_2\text{CH}_2\text{N} - \text{CH}_2\text{PO(OX)}_2 \]

2. Trimethylene diamine tetra(methylene phosphonic acid) and salts thereof

\[ (\text{OX})_2\text{OPCH}_2 \quad \text{N} - \text{CH}_2\text{CH}_3\text{N} - \text{CH}_2\text{PO(OX)}_2 \]

3. Dodecamethylene diamine tetra(methylene phosphonic acid) and salts thereof

\[ (\text{OX})_2\text{OPCH}_2 \quad \text{N} - \text{CH}_2\text{CH}_{12}\text{N} - \text{CH}_2\text{PO(OX)}_2 \]

4. Hexamethylene diamine di(methylene phosphonic acid) and salts thereof

\[ (\text{OX})_2\text{OPCH}_2\text{NH} - \text{CH}_2\text{NHCH}_2\text{PO(OX)}_2 \]

5. N-oleylamine di(methylene phosphonic acid) and salts thereof

\[ \text{H}_3\text{C}_18\text{N} - \text{CH}_2 - \text{PO(OX)}_2 \]
(6) diethylene triamine penta(methylene phosphonic acid) and salts thereof

(7) ethanol amine di(methylene phosphonic acid) and salts thereof

(8) n-hexyl amino(isopropylidene phosphonic acid) (methyl phosphonic acid) and salts thereof

(9) sulfonylethylene amino di(methylene phosphonic acid) and salts thereof

(10) 1-hydroxyethylidene-1,1-diphosphonic acid and salts thereof

(11) amino tri(methylene phosphonic acid) and salts thereof

The dispersing aids described herein are either commercially available or readily prepared using known preparatory methods. Examples of such methods are described, for example, in U.S. Patents 3,288,846 and 3,298,956, mentioned hereinbefore, as well as in U. S. Patents 3,214,454, issued October 26, 1965; 3,234,124, issued February 8, 1966; 3,567,768, issued March 2, 1971; and 3,796,749, issued March 12, 1974. Similarly, the other components of the pigment layer forming composition, i.e. the film-forming binders and pigments, are also either commercially available or readily prepared by workers of ordinary skill in the photographic chemistry art.

The coating composition used to form a pigmented layer in this invention is typically an aqueous-based composition. Preferably, the liquid medium is water. However, mixtures of water and water-miscible organic solvents (e.g. alcohols and ketones) can be used as long as water comprises at least 50 weight percent of the mixture.

The components of the pigmented coating composition can be mixed together in any suitable manner for forming a uniform pigment dispersion. Generally, to obtain a uniform pigment dispersion, pigment and dispersing aids are slowly added to the
liquid medium (e.g. water) and dispersed with mixing or dispersing equipment, such as a commercially-available mill. This addition is typically done at ambient conditions over a period of from about 5 to about 30 minutes. Although the weight percent solids of this dispersion can vary widely, generally it is in the range of from 50 to 80 percent, preferably 70 to 75 weight percent. The duration of mixing of the dispersion may vary, but it is generally completed in a period of up to 45 minutes, although a longer period of mixing is not harmful.

The pigmented dispersion is then gradually mixed with the binder, either by adding the dispersion to the binder or vice versa. Preferably, the dispersion is gradually added to a binder solution (e.g. gelatin in water) under high shear conditions at an elevated temperature typically in the range of from 35 to 60°C. Although it can vary widely, the weight percent of solids in the binder solution is typically in the range of from 35 to 55 percent. The binder solution contains a liquid medium, such as water, and can also contain additional pigment in an amount typically of from 1 to 25 weight percent, based on total solution weight. If necessary, the pH of the resulting coating composition can be adjusted with a suitable acid or base to within the range of from 5 to 9. Agitation is then applied to the coating composition to completely mix all components.

Although the amounts of the described components of the coating composition can be varied widely to achieve desired properties, the typical and preferred amounts are as follows, based on total composition solids (i.e. dry weight). The pigment to binder ratio is typically in the range of from 2.5:1 to 40:1, and preferably from 10:1 to 30:1. The amount of dispersing aid present is typically in
the range of from 0.05 to 2, and preferably from 0.1 to 0.5, weight percent based on dry pigment weight.

In addition to the essential components described herein, the coating composition can also contain one or more other addenda common to pigmented coating compositions. Such addenda include, but are not limited to, wetting aids, surface active agents, brighteners, ultraviolet light absorbers, stabilizers, hardeners, colorants, coating aids, binder extenders, defoamers, biocides, and the like. These addenda can be present in quantities typically used in the art.

The coating composition can be used to form a pigmented layer or layers in any image-forming or image-receiving element where there is a desire to provide a highly reflective layer on a support. Generally, such image-forming elements include photographic elements, such as those used to provide reflection prints (both color and black-and-white), including photographic "papers" (having paper or resin substrates), phototypesetting elements and diffusion transfer or image transfer film units. Typical image-receiving elements include receiver sheets used in two-sheet diffusion or image transfer products. The characteristics and components of such image-forming and image-receiving products and methods of making them are known in the art. Typical references describing such elements, components thereof and methods of making them include Research Disclosure, publication 17643, U. S. Patents 3,501,298, issued March 17, 1970, 3,635,713, issued January 18, 1972, 3,755,069, issued August 28, 1973, 3,833,380, issued September 3, 1974, and 3,936,304, issued February 3, 1976 and U. K. Patent Application 2,078,235A, published

The elements of this invention require a support. Sometimes such supports are laminates of one or more layers. Typical supports include polymeric films (e.g. cellulose nitrate, polyesters, polyamides and cellulose esters), wood fiber or cellulosic substrates (e.g. paper), metallic sheets and foils, glass and ceramic substances.

Preferably, the elements of this invention have a support which comprises a cellulosic base substrate made from raw paper stock. These preferred supports also have a baryta or thermoplastic resin layer on either or both sides of the cellulosic base substrate. More preferably, they have a continuous thermoplastic resin layer on each side of the cellulosic base substrate. One or both of these thermoplastic resin layers can contain a white pigment. Typical useful thermoplastic resins include polyolefins such as polyethylene, polypropylene, mixtures thereof and polystyrene. A more detailed description of useful supports, both polymeric and cellulosic, their components (e.g. pigments, stabilizers, antioxidants and sizes) and methods of making them is provided in Research Disclosure, publication 17643, paragraph XVII, and the references mentioned in that publication.

The image-forming elements of this invention comprise one or more image-forming layers situated on the support. Such layers include
suitable image-forming materials which are sensitive to heat, actinic radiation of appropriate wavelength or electrical energy, depending upon the method of imaging used. The components of such image-forming materials are described, for example, in the references listed herein with respect to the elements in general. The photosensitive components of such layers can be silver halides, diazonium compounds and other light sensitive materials within the skill of a worker in the art as described, for example, in Research Disclosure, publication 17643.

The image-receiving elements of this invention have one or more image-receiving layers located on the support. Such layers "receive" an image from one or more image-forming layers in the same or different element. Image-receiving elements are sometimes known as "receivers" and are useful, for example, in the two-sheet diffusion transfer products described hereinbefore.

Optionally, the elements of this invention can comprise additional layers, such as subbing, antihalation, antistatic, conductive, adhesive, protective, sizing and other suitable layers as is known in the art. The typical thicknesses, composition and location of such layers are also known in the art.

The pigmented layers used in the elements of this invention can be formed by applying the pigmented coating composition in any suitable way. The composition is applied by any suitable coating technique using appropriate coating equipment. The pigment layer is located between the support and the image-forming or image-receiving layer. Preferably, the pigment layer is adjacent to the support, although this location is not essential. Often the
pigment layer is located adjacent to the inner resin coating of a photographic paper support.

To further illustrate the location of the pigment layers, reference is made to the drawings:

In FIG. 1, image-forming element 10 comprises a support 11 and image-forming layer 12.
Pigment layer 13 is located between support 11 and image-forming layer 12.

In FIG. 2, image-receiving element 20 has a support 21 and an image-receiving layer 22, between which is located pigment layer 23.

In FIG. 3, photographic element 30 comprises a support 31 which includes a cellulosic base substrate 32 which has continuous thermoplastic resin layers 33 and 34 on either side thereof.

Adjacent to support 31 is a pigment layer 35 containing a white inorganic pigment such as rutile titanium dioxide, gelatin and an organopolyphosphonic acid or salt dispersing aid. A photosensitive image-forming layer 36 is located adjacent to pigment layer 35 on the surface opposite support 31.

The following Example further illustrates the invention.

Example

Preparation of Pigment Coating Compositions

An aqueous pigment dispersion was prepared by mixing the following components for 45 minutes at ambient conditions in a commercially-available mill.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Parts per hundred (weight)</th>
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<tr>
<td>Rutile titanium dioxide</td>
<td>70</td>
</tr>
<tr>
<td>Pentasodium salt of amino tri(methylene phosphonic acid) (40% active)</td>
<td>0.41</td>
</tr>
<tr>
<td>Biocide (3.5% active)</td>
<td>0.26</td>
</tr>
<tr>
<td>Distilled water</td>
<td>29.33</td>
</tr>
</tbody>
</table>

Total: 100.0
An aqueous binder solution containing the following components was similarly prepared.

<table>
<thead>
<tr>
<th>Parts per hundred (weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rutile titanium dioxide</td>
</tr>
<tr>
<td>Acid-processed gelatin</td>
</tr>
<tr>
<td>Distilled water</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

The pigment dispersion was then gradually added to the binder solution at 43°C over a period of 15 minutes. The pH of the resulting composition was adjusted to between 5.4 and 5.8 with sulfuric acid. The composition was continually mixed in the commercially available mill during and subsequent to the addition of the pigment dispersion for about 45 minutes to uniformly disperse the pigment therein. No pigment agglomeration was observed. This composition is designated Composition I hereinafter.

For comparison, a pigmented coating composition (designated Composition II hereinafter) using the sodium polymethacrylate as the dispersing aid, as described in the art previously discussed herein, was prepared with the following components using the techniques described previously in this Example.

<table>
<thead>
<tr>
<th>Parts per hundred (weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rutile titanium dioxide</td>
</tr>
<tr>
<td>Sodium polymethacrylate dispersing aid</td>
</tr>
<tr>
<td>Biocide (3.5% active)</td>
</tr>
<tr>
<td>Acid-processed gelatin</td>
</tr>
<tr>
<td>Distilled water</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>
As the pigment was added to the gelatin solution, pigment agglomeration was observed. Additional agglomeration was observed when the pH of the composition was adjusted to 5.8.

Preparation of Elements

Compositions I and II were each coated to form pigment layers in respective photographic elements. These elements comprised polyethylene resin-coated paper supports and photosensitive color emulsion layers similar to those described, for example, in U. S. Patent 3,833,380, issued September 3, 1974. The coverage for the respective pigment layers was about 6.63 g of pigment composition per square meter of surface. The pigment to binder ratio was between 27:1 and 31:1.

Control A element was prepared without a pigment layer. Control B and C elements were each prepared from Composition II with a pigment layer adjacent to the polyethylene resin coating of the paper support between the support and the photosensitive layers. The pigment layer and the photosensitive layers of the Control B element were coated in separate coating operations. In other words, the pigment layer was coated onto the support and the photosensitive layers were subsequently coated onto the pigment layer. In preparing the Control C element, the pigment layer was coated simultaneously with the photosensitive layers in a multilayer coating operation.

Element D was prepared with a pigment layer applied from coating Composition I. In this preparation, the pigment layer was coated simultaneously with the photosensitive layers.
Properties

Data relating to the characteristics of the pigmented layers and elements containing them are presented in Table I below. The test conditions and a discussion of the results follow the table.

Table I

<table>
<thead>
<tr>
<th>Test</th>
<th>Control A</th>
<th>Control B</th>
<th>Control C</th>
<th>Control D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Multiple arm scribe test</td>
<td>20</td>
<td>11</td>
<td>13</td>
<td>29</td>
</tr>
<tr>
<td>Adhesion test</td>
<td>1</td>
<td>4</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Cracking test (number of cracks) before development</td>
<td>12</td>
<td>43</td>
<td>8</td>
<td>0</td>
</tr>
<tr>
<td>after development</td>
<td>8</td>
<td>39</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Reticulation test</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>air dried</td>
<td>4</td>
<td>5</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>after incubation</td>
<td>4</td>
<td>5</td>
<td>5</td>
<td>N.P.**</td>
</tr>
<tr>
<td>Filterability test</td>
<td>N.P.**</td>
<td>N.P.**</td>
<td>4%</td>
<td>100%</td>
</tr>
<tr>
<td>Gloss test</td>
<td>N.P.**</td>
<td>12</td>
<td>N.P.**</td>
<td>84*</td>
</tr>
</tbody>
</table>

* test performed on coating made on paper support without photosensitive layers

** test was "not performed" for the given element

Test Conditions

In the multiple arm scribe test, a plurality of weighted prongs are allowed to move down a moving, wet sample of imagewise exposed and developed photographic element until the prongs break the surface of the imaged layers. This test is a measure of hardness of the layers on the support. A value greater than 20 is acceptable.
The adhesion test is a subjective test to determine if the wet exposed and developed imaged layers and pigment layers adequately adhere to the paper support. While the layers are wet with developer, an attempt is made to rub them off of a sample of the element by hand. A value of 1 is acceptable for this test. The higher values indicate more imaged layer and underlying layers were rubbed off.

In the cracking test, a 2.54 cm. wide sample of element is conditioned at 38°C and 12% relative humidity for 30 minutes. One end of the sample is then attached to a 350 g. weight and the opposite end is wrapped around a cylinder which is 0.953 cm. in diameter, image-forming layers outward. The number of cracks per unit area found at a specified spot on the sample are than counted.

The reticulation test is a subjective evaluation of the number of fine cracks evident in the outer surface of a fully exposed and developed sample with no stress being placed on it. As agglomerations in the pigment layer increase, so does the level of reticulation. A rating of 1 to 5 is given to each sample with 1 representing very little reticulation. An air-dried sample is allowed to dry in the air after development. Incubated samples are subjected to 49°C and 50% relative humidity for 6 days.

The filterability test measures the percentage of a 500 g. sample of pigment coating composition which can be filtered through a 3.8 cm. diameter filter having approximately 15,000-20,000 millimeters pore size in 1 minute. It is desired that the filterability of a pigment composition be
as high as possible. The less the number of agglomerations, the higher the percent filterability.

The gloss test measures the percent reflectance from light incident at a 75° angle from normal to the surface per the standard TAPPI test T408-OS-78. The less the number of agglomerations, the higher the gloss. This test is commonly known as the Gardner gloss test.

Discussion of Results

The pigmented composition and element of Element D exhibited significant improvements over the Controls in several important characteristics. Thus, Element D exhibited significantly improved hardness, as shown by the higher multiple arm scribe test results. The hardness result of Control A was borderline and that of each of Control B and C was unacceptable. Also, Element D exhibited a significant improvement in resistance to stress cracking in comparison to Controls A, B and C.

Although Control C showed an improvement with respect to Controls A and B, Element D was clearly superior.

It should also be noted that Composition I was much more filterable than the Control Composition II which contained many pigment agglomerations. Element D also exhibited a significant improvement in resistance to cracking and gloss over the Control B element. In addition, Element D exhibited improved image sharpness when imagewise exposed and developed in comparison to similarly treated samples of Control elements B and C. Moreover, Element D showed some improvement over all or some of Controls A, B and C in the adhesion and reticulation tests.

Similar improved results can be obtained when the pentasodium salt of amino tri(methylene
phosphonic acid) is substituted with other organopolyphosphonic acid or salt dispersants such as ethylene diamine tetra(methylene phosphonic acid) and salts thereof, n-oleylamine di(methylene phosphonic acid) and salts thereof, ethanol amine di(methylene phosphonic acid) and salts thereof, sulfonyl ethylene amino di(methylene phosphonic acid) and salts thereof, 1-hydroxyethylidene-1,1-diphosphonic acid and salts thereof.
Claims:

1. An element comprising a support having thereon a layer that (a) comprises a film-forming binder, a pigment and a dispersing aid for the pigment and, (b) is located between the support and an image-forming or image-receiving layer, characterized in that the dispersing aid is an organopolyphosphonic acid or salt.

2. The element of claim 1, wherein the dispersing aid is an organoaminopolyphosphonic acid or salt.

3. The element of either of claims 1 or 2, wherein the dispersing aid is present in an amount of from 0.1 to 2 percent, based on the dry weight of the pigment, and the weight ratio of the pigment to the binder is from 2:1 to 20:1.

4. The element of any of claims 1-3 wherein the layer comprising dispersing aid is located between the support and an image-forming layer.

5. The element of any of claims 1-4 wherein the support comprises a cellulosic base substrate having on each side thereof a thermoplastic resin layer.

6. The element of any of claims 1-5 wherein the pigment layer is adjacent to the support.

7. The element of any of claims 1-6 wherein the film-forming binder is a hydrophilic colloid and the pigment is a white inorganic pigment.

8. The element according to any of claims 1-3 and 5-7 wherein the layer comprising dispersing aid is located between the support and an image-receiving layer.
9. The element of any of claims 1-8 wherein the image-forming layer is a photosensitive silver halide emulsion layer and the pigment is titanium dioxide.
INTERNATIONAL SEARCH REPORT

International Application No. PCT/US 83/01415

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) 1

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC\(^3\): G 03 C 5/54; G 03 C 1/84

II. FIELDS SEARCHED

Classifications System Minimum Documentation Searched 4

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Documentation Searched other than Minimum Documentation to the extent that such Documents are Included in the Fields Searched 4

III. DOCUMENTS CONSIDERED TO BE RELEVANT 14

<table>
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<tr>
<th>Category *</th>
<th>Citation of Document, 14 with indication, where appropriate, of the relevant passages 17</th>
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<td>DE, A, 2611768 (BAYER) 22 September 1977, see claims; page 5, lines 18-24</td>
<td>1-9</td>
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<tr>
<td>Y</td>
<td>DE, A, 1542202 (HENKEL &amp; CIE.) 29 January 1970, see claims</td>
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</table>
| P,Y        | Research Disclosure, November 1976
             | Industrial Opportunities Homewell, Hampshire (GB) disclosure no. 15126             |
             | "Photographic processes and products"                                            |
             | pages 75-87, see page 82, right-hand column                                       | 1-9                    |
| A          | DE, A, 3015023 (THE WIGGINS TEAP) 6                                              |
             | November 1980, see the claims                                                    | 1                      |
| A          | US, A, 3713859 (M.F. HOOVER et al.) 30                                           |
             | January 1973, see the claims                                                     | 1                      |

* Special categories of cited documents: 13
- **A** document defining the general state of the art which is not considered to be of particular relevance
- **E** earlier document but published on or after the international filing date
- **L** document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another document, or other special reason (as specified)
- **O** document referring to an oral disclosure, use, exhibition or other means
- **P** document published prior to the international filing date but later than the priority date claimed

**T** later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

**X** document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

**Y** document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

**A** document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search 9

21st December 1983

International Searching Authority 1

EUROPEAN PATENT OFFICE

Date of Mailing of this International Search Report 8

16 JAN. 1984

Signature of Authorized Officer 80

G.L.M. Kruycamp
ANNEX TO THE INTERNATIONAL SEARCH REPORT ON
INTERNATIONAL APPLICATION NO. PCT/US 83/01415 (SA 5819)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 10/01/84.

The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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US-A- 3713859 | 30/01/73 | None |

For more details about this annex: see Official Journal of the European Patent Office, No. 12/82.