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⑤④ **Acidic adhesive compositions and image recording products containing same.**

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Description

This invention relates to acidic adhesive compositions which are useful in the image-recording field. In particular, it relates to mask adhesive compositions which provide high strength bonds in image-forming elements while greatly improving border quality around image areas. This invention also relates to image-recording elements and particularly to self-processing film units, containing such adhesive compositions.

Image-recording elements having a mask that forms a border and includes, at least in part, a latent or visible image, are well known in the photographic art. Typical elements of this type are self-processing photographic products which are generally referred to in the photographic art as diffusion transfer, image transfer or instant photographic film units.

In some of these units, an image-receiving layer provides a viewable image and can be separated from an image-recording layer(s) after processing. In others, the image-receiving layer(s) can remain permanently attached and integral with the image-recording layer and layers ancillary thereto when a transparent support is employed on the viewing side of the unit. After exposure of the film unit, an alkaline processing composition permeates the various layers to initiate development of the exposed image-recording layers. This processing composition can be introduced from outside the film unit or from a container or rupturable pouch associated with the film unit. In most instances, conventional darkroom processes and after-treatments, such as washing and stabilization are not needed to provide an acceptable image since the film unit is fully self processing.

In a typical self-processing photographic film unit the mask is a thin framing means which is bonded to layers or components above and below it with various adhesives. For example, U.S. Patent 3,256,090 issued June 14, 1966, describes the use of encapsulated, low-strength adhesives to temporarily bond the mask to an image-receiving layer while acidic polyester mask adhesives that provide permanent bonds in film units are described in U.S. Patent 4,097,282 issued June 27, 1978, and non-acidic polyester mask adhesives are described in U.S. Patent 4,113,493 issued September 12, 1978. The mask provides a border around an aperture which is adapted to receive the alkaline processing composition. The border also defines an image, or picture area. Usually, the mask is located between and around the edges of two components of the film unit (e.g. cover sheet and photosensitive element) to provide a space or cavity between the components for the processing composition. The edge of the mask around the aperture restricts the processing composition to the image area and confines the resulting image to such area.

It has been the aim of workers in the photographic art to improve border quality in image-recording elements, particularly the self-processing film units described herein. Border quality denotes relative freedom from visible imperfections in the border around the aperture. Such imperfections include lines, spots, stains and dye deposits. Unfortunately, these workers have had very limited success in improving border quality since a modification that may remove one imperfection may amplify another. The addition of various materials to various layers of the film unit to reduce imperfections is not always possible because such materials may cause sensitometric problems. Some imperfections are caused by manufacturing procedures which cannot be adequately modified to remove the imperfections.

A serious imperfection often found in the borders of prior art self-processing film units is known as "border bleed". This imperfection causes the border to appear colored (e.g. cyan) instead of white and to blend into the image area. Border bleed is believed to result from the lateral migration of color-forming dyes or dye-providing materials (e.g. dye releasers) from the image area into the border during or after processing of image-recording layers. Such migration is accelerated when a film unit is subjected to elevated temperatures (e.g. 30—60°C) or high humidity after processing for extended periods of time.

Another imperfection observed in some film units after processing has begun is known as "dark edge line". This imperfection is a single or series of parallel dark lines, continuous or segmented, in the border at the edge of the image area. Dark edge line apparently forms in the following way. When alkaline processing composition is introduced into the image area, some of it moves laterally in the image-recording layers into the border "under" the mask. Dyes are caused to be released by the composition as it moves into the border. These dyes diffuse to the image-receiving layer and form objectionable darkened deposits (e.g. dark lines) in the border at the edge of the image area.

Dark edge line is intensified by the presence of air (in the form of "pockets" or "bubbles") which can occur at the border-image area interface. Oxygen within the bubbles causes dye to be released. This dye diffuses to the image-receiving layer and forms dye deposits. The aforementioned air pockets or bubbles can result from nucleation of bubbles at the mask-mask adhesive interface, or from voids in the adhesive. Bubble nucleation and voids can result from nonuniform sealing between mask and image-recording layers which often occurs during conventional manufacturing operations. Air bubbles can also result when the manufactured film units are subjected to stress in handling, shipping and use (e.g. twisting, bending, etc.). Such stressful conditions are very difficult to monitor and control, especially after the film units are in the hands of consumers.

The dark edge line imperfection becomes more pronounced when image development is allowed

to or necessarily proceeds for relatively longer periods of time (e.g. in winter time or in colder climates). Yet such long development times may be desirable or necessary in certain situations with certain image-recording materials.

Some reduction in border bleed has been achieved by adding certain acidic terpolymers to gelatin interlayers or titanium dioxide reflective layers of self-processing photographic film units, as described in *Research Disclosure*, publication 19146, March, 1980 (published by Industrial Opportunities, Ltd., Homewell, Havant Hampshire PO9 1EF United Kingdom). However, this reference fails to teach or suggest the present invention which provides an improvement in overall border quality by simultaneously and significantly reducing both border bleed and dark edge line imperfections. Moreover, we have determined that positioning terpolymers in interlayers or reflective layers as described in the *Research Disclosure* publication can undesirably lengthen access time, i.e. the time required for image formation.

From the foregoing discussion, it is clear that there is a significant problem with imperfections in the borders of image-recording materials (e.g. self-processing film units). An improvement in border quality, particularly with regard to border bleed and dark edge line, would obviously enhance the aesthetic qualities of processed film units (i.e. finished prints) while permitting extended development or storage time of unprocessed film units.

The present invention provides image-recording elements which exhibit excellent border quality. This is achieved by the use of a new mask adhesive composition which simultaneously provides high strength permanent bonds and improved border quality. This composition is an acidic polymeric adhesive composition characterized in that it comprises a polymeric acidic component having at least three milliequivalents of acid per gram of such component, and a substantially immobile, blocked photographic development restrainer or a substantially immobile, blocked competing photographic developer.

The image-recording elements of this invention which exhibit excellent border quality comprise:

- 1) a support
- 2) a plurality of layers including an image-recording layer having an image area adapted to be processed by an alkaline processing composition, and
- 3) a mask providing an aperture adapted to receive the alkaline processing composition and a border which defines the image area.

The mask is permanently bonded directly or indirectly to the image-recording layer by a high strength adhesive composition which is disposed within the border and is subject to contact with the alkaline processing composition.

This element is characterized in that the adhesive composition comprises a polymeric acidic component that is adapted to neutralize the alkaline processing composition in the border and has at least 3 milliequivalents to acid per gram of the acid component, and a substantially immobile, blocked photographic development restrainer or a substantially immobile, blocked competing photographic developer.

In self-processing image-recording elements prepared according to this invention, the plurality of layers referred to in the preceding description can include an image-receiving layer, as described herein.

Figure 1 is a front plan view of a self-processing film unit of this invention, partly cut away to show a portion of the inner construction.

Figure 2 is a rear plan view of the film unit illustrated in Figure 1, partly cut away to show portions of the inner construction.

Figure 3 is an exaggerated partial, sectional view taken along line 3—3 of Figure 2.

Figure 4 is a perspective view of equipment which does not form a part of this invention but is used to determine bond strengths of adhesives adhering a mask and another material as described in the following Examples.

As previously indicated, an essential ingredient of the adhesive compositions of this invention is a polymeric acidic component which has at least 3 milliequivalents of acid per gram of component. This component includes one or more acidic polymers. As used herein the term "acidic polymer" refers to a polymer having acid groups, such as carboxy, sulfo, phosphono or sulfino groups. Many such acidic polymers are known, as described for example, in U.S. Patent 3,362,819 issued January 9, 1968, and *Research Disclosure*, publication 13525, July, 1975 (published by Industrial Opportunities, Ltd., Homewell, Havant Hampshire, PO9 1EF United Kingdom).

The acidic polymers useful in practicing this invention are typically condensation or addition polymers which have the desired adhesive and neutralizing capabilities. The adhesive compositions exhibit a bond seal strength of at least 441 N/m (450 g/cm), and preferably at least 578 N/m (590 g/cm), as measured by performing 180° peel tests on a commercially available Instron (trade mark) Tensile Tester, Model 1101 or 1130 (Instron Corp. of Canton, Mass., U.S.A.). Adhered samples for peel tests are prepared in advance by sealing a mask material to various substrates such as a photo-sensitive element, using heat and pressure. A more detailed description of the peel tests and equipment used is given hereinafter immediately preceding the Examples.

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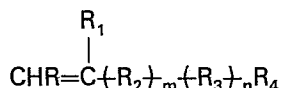
The adhesive compositions of this invention are preferably used as mask adhesives in image-recording elements where these adhesives are open or exposed to contact with alkaline processing compositions. In other words, the mask adhesives are subject to contact with the alkaline processing compositions during processing of the image area.

5 The acidic polymers useful in this invention generally have inherent viscosities in the range of from 0.3 to 1.5, and preferably from 0.35 to 1.0, as measured at 25°C in a suitable solvent, such as dioxane or a pH 5 buffer solution, at a concentration of 0.25 g/dl of solution. For example, the inherent viscosities of poly(n-butyl acrylate-co-acrylic acid) (30:70 weight ratio) and poly(n-butyl acrylate-co-2-acrylamido-2-methylpropane-sulfonic acid) (25:75 weight ratio) used in the following Examples to
10 illustrate the invention were in the range of 0.55—0.75 in dioxane and 0.33—0.5 in a pH 5 buffer solution, respectively. As used herein, inherent viscosity is determined by the formula:

$$(\eta) = \frac{2.30 \log \eta\mu}{c}$$

where (η) is the inherent viscosity, $\eta\mu$ is the relative viscosity, i.e. the viscosity of a solution of the polymer in the solvent divided by the viscosity of the solvent in the same units, and c is the concentration in grams of polymer per 100 ml. of solution.

20 A class of acidic polymers useful in this invention comprises from 5 to 90 percent, often 45 to 85 percent, by weight, of units derived from one or more acidic monomers of the formula (I):



wherein each of m and n is 0 or 1. Each of R and R_1 is hydrogen; methyl; halo, e.g. fluoro, chloro or bromo; or a monovalent acidic radical, e.g. carboxy. Preferably, each of R and R_1 is hydrogen or methyl, and most preferably, each is hydrogen.

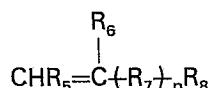
30 R_2 is oxy, carbonyl, carbonyloxy or carbonylimino. R_3 is a divalent aliphatic, alicyclic or aromatic radical containing carbon and hydrogen, and optionally, oxygen atoms. More preferably, R_3 is a divalent hydrocarbon, typically of 1 to 20 carbon atoms, such as alkylene, arylene, cycloalkylene, arylene-alkylene, alkylenearylene or arylenebisalkylene. Specifically, R_3 can be alkylene, typically of 1 to 12 carbon atoms, such as methylene, ethylene, propylene, 2,2-dimethyl-1,3-propylene, 1,1-dimethyl-ethylene, 2-methyl-1,3-propylene or decylene; or arylene, typically of 6 to 18 carbon atoms, such as phenylene, naphthylene or xylylene.

35 R_4 is a monovalent acid radical, such as carboxy, sulfo, phosphono or sulfinio; alkyl, typically of 1 to 6 carbon atoms, e.g. methyl, 2-methylpropyl or hexyl; or alkoxy-carbonyl, typically of 2 to 7 carbon atoms, e.g. methoxycarbonyl. When R_4 is alkyl or alkoxy-carbonyl, at least one of R or R_1 is a monovalent acid radical, such as carboxy.

40 Acidic monomers which are useful in the practice of this invention are acrylic acid, methacrylic acid, aconitic acid, acryloyloxypropionic acid, citraconic acid, chlorofumaric acid, fumaric acid, itaconic acid, maleic acid, α -methyl glutaric acid, crotonic acid, 2-acrylamido-2-methylpropanesulfonic acid, 2-methylacrylamido-2-methylpropane-sulfonic acid, 3-acryloyloxy-butanedisulfonic acid, vinylsulfonic acid, methacryloyloxyethyl-1-sulfonic acid and p-styrene sulfonic acid. The acidic monomers useful herein are commercially available or can be readily prepared by suitable techniques known to a person of ordinary skill in the art.

45 In addition, the acidic polymers described hereinbefore can comprise from 10 to 95 percent, often 15 to 55 percent, by weight, of units derived from one or more additional polymerizable, ethylenically unsaturated monomers. Any such monomer or monomers can be used as long as the resulting acidic polymer has the neutralizing and adhesive capabilities which have been described previously in this specification. The additional monomer(s) can provide crosslinking capability to the polymer if desired.

Typical additional ethylenically unsaturated monomers are represented by the formula (II):

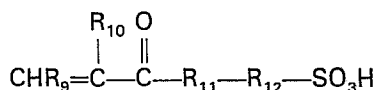


55 wherein p is 0 or 1. Each of R_5 and R_6 is hydrogen, methyl or halo, e.g. fluoro, chloro or bromo. R_7 is carbonyl, carbonyloxy or carbonylimino.

60 R_8 is hydrogen or a monovalent aliphatic, alicyclic or aromatic radical containing carbon and hydrogen, and optionally, oxygen atoms provided, however, when R_8 is hydrogen and p is 1, R_7 is carbonylimino. Preferably, R_8 is a monovalent hydrocarbon, typically of 1 to 20 carbon atoms, such as alkyl, including aralkyl, aryl including alkaryl, allyl or cycloalkyl. Most preferably, R_8 is alkyl, typically of 1 to 12 carbon atoms, such as methyl, ethyl, isopropyl, n-butyl, decyl or lauryl.

Exemplary monomers having formula (II) are n-butyl acrylate, *trans*-1,2-dichloroethylene, 2-norbornylmethyl methacrylate, ethyl 2-chloromethacrylate, methyl acrylate, n-lauryl methacrylate, N-isopropylacrylamide, acrylamide and vinyl acetate. These monomers are commercially available or can be readily prepared by suitable techniques known to a person of ordinary skill in the art.

In practicing this invention, it is advantageous to use an adhesive composition comprising an acidic polymer in which the acidic monomer units of the formula (I) are derived from the class of sulfo-containing monomers having the formula (III):



wherein each of R_9 and R_{10} is hydrogen, methyl or halo; e.g. fluoro, chloro or bromo; R_{11} is oxy or imino; and R_{12} is alkylene, typically of 1 to 12 carbon atoms, e.g. methylene, ethylene, propylene, trimethylene, 1,1-dimethylethylene, 2,2-dimethyl-1,3-propylene, 2-methyl-1,3-propylene or decylene or arylene, typically of 6 to 18 carbon atoms, such as phenylene, naphthylene or xylylene. In comparison to the other acidic polymers described herein, these sulfo-containing polymers provide adhesives that exhibit a significant decrease in heat sealing temperatures without sacrificing the excellent border quality and bond strengths described herein. This provides an improvement in heat sealing latitude which enables a user to achieve marked reductions in manufacturing costs. For example, expensive changes in existing sealing equipment are avoided. Also, such sulfo-containing polymeric adhesive compositions make it possible for a user to seal less heat resistant materials. Further, and of great significance to our energy-conscious society, one who uses these adhesive compositions needs less energy for sealing operations. Moreover, the aforementioned improvement in heat sealing latitude was quite unexpected since the sulfo-containing polymers useful in this invention have considerably higher glass transition temperatures (T_g) than acidic polymers, such as the carboxy-containing polymers described herein. In view of this higher T_g , the sulfo-containing polymers would be expected to be sealed at relatively higher temperatures. Yet, just the opposite is the case. As illustrated in the following examples, particularly Examples 4 and 5; the adhesive compositions containing sulfo-containing polymers as described herein, can be sealed at temperatures which are significantly lower than the sealing temperatures used with compositions containing other acidic polymers, e.g. carboxy-containing polymers. As used herein, T_g can be determined by differential scanning calorimetry, as disclosed in Techniques and Methods of Polymer Evaluation, Vol. 2, Marcel Dekker, Inc. N.Y. 1970.

Examples of monomers of formula (III) are 2-acrylamido-2-methylpropanesulfonic acid, 2-methacrylamido-2-methylpropane-sulfonic acid, 2-acrylamidoethanesulfonic acid, 3-acryloyloxybutanesulfonic acid, 3-acryloyloxypropanesulfonic acid and 2-acryloyloxyethanesulfonic acid. These and similar sulfo-containing monomers are commercially available or can be readily prepared by suitable techniques known to a person of ordinary skill in the art.

As previously indicated, acidic polymers useful in the adhesive compositions of this invention can comprise units derived from two or more acidic monomers. A particularly useful acidic polymer of this type has units derived from a carboxy-containing monomer and a sulfo-containing monomer of formula (III). In such a polymer, it is preferred that from 5 to 50 percent, by weight, of the units be derived from the sulfo-containing monomers of formula (III). Examples of suitable sulfo-containing polymers of this type comprise:

- (a) from 5 to 50 percent, by weight, of units derived from a sulfo-containing monomer of formula (III) described hereinabove;
- (b) from 10 to 85 percent, by weight, of units derived from a carboxy-containing polymerizable ethylenically unsaturated monomer; and
- (c) from 10 to 40 percent, by weight, of an additional polymerizable ethylenically unsaturated monomer, such as of formula (II) described hereinabove.

Representative acidic polymers useful in this invention are poly(methyl acrylate-*co*-acrylic acid), poly(n-butyl acrylate-*co*-acrylic acid), poly(vinyl acetate-*co*-acrylic acid), poly(n-lauryl methacrylate-*co*-acrylic acid), poly(n-butyl methacrylate-*co*-3-methacryloyloxypropanesulfonic acid), poly(N-isopropylacrylamide-*co*-acrylic acid), poly(methyl methacrylate-*co*-n-butyl acrylate-*co*-acrylic acid), poly(n-butyl acrylate-*co*-2-acrylamido-2-methylpropanesulfonic acid) and poly(n-butyl acrylate-*co*-acrylic acid-*co*-2-acrylamido-2-methylpropanesulfonic acid) poly(ethyl methacrylate-*co*-acrylamide-*co*-2-acrylamido-2-methylpropanesulfonic acid), and poly(N-isopropylacrylamide-*co*-2-acrylamidoethanesulfonic acid).

The polymeric acidic component described herein can be a mixture of acidic polymers, such as preferably, a mixture of one or more sulfo-containing polymers and one or more carboxy-containing polymers, e.g. a carboxy-containing linear addition polymer. Typical sulfo-containing polymers are those having units derived from one or more monomers of formula (III). Such mixtures can contain from 1 to 99 weight percent, and preferably from 30 to 80 weight percent of the sulfo-containing polymer(s), based on total polymeric acidic component weight. A preferred mixture of acid polymers

which can be used in practicing this invention is a mixture of poly(n-butyl acrylate-co-acrylic acid) with poly(n-butyl acrylate-co-2-acrylamido-2-methylpropanesulfonic acid).

The polymerization conditions which can be used for making polymers useful in this invention are those commonly employed in condensation and addition polymerization techniques known in the art. For the preferred addition polymers, these techniques include suspension and solution techniques. In these techniques, polymerization temperature is subject to wide variation as it depends upon several variables, but it is generally in the range of from 20° to 120°C. The pressure employed in the polymerization, if any, is usually only sufficient to maintain the reaction mixture in liquid form. The polymerization can be carried out in a suitable vehicle, for example, in water or mixtures of water with water miscible solvents, e.g. methanol, ethanol, propanol, isopropanol or butanol, or in an organic solvent or in mixtures of organic solvents, e.g. N,N-dimethylformamide, acetone, dimethyl sulfoxide, tetrahydrofuran or methoxyethanol. Generally, the concentration of polymer in solution or suspension is up to 40%, by weight, and preferably from 10 to 25%, by weight, based on the total weight. Suitable catalysts include free radical catalysts, e.g. hydrogen peroxide, cumene hydroperoxide or water-soluble azo type initiators. Suitable non-ionic, ionic and amphoteric surface active agents can be used if desired. In redox polymerization systems, the conventional ingredients can be employed. If desired, the polymer can be isolated from the reaction medium by freezing, salting out, precipitation or any other suitable procedure.

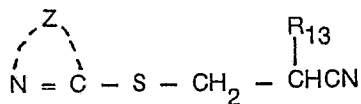
The concentration of polymeric acidic component in the adhesive compositions of this invention is generally in the range of from 70 to 96 percent and preferably, from 80 to 90 percent, by weight. In a dried adhesive layer of from 0.002 to 0.013 mm (0.1 to 0.5 mils) thick, the coverage of polymeric acidic component is generally from 2 to 12 g/m² (0.2—1.2 g/ft²), and preferably from 3 to 7 g/m² (0.3—0.65 g/ft²), of surface area. Although the polymeric acid component of the adhesive composition must have at least 3 milliequivalents of acid per gram, such component preferably has 3 to 12 milliequivalents of acid per gram. Accordingly, the specific polymeric acids employed to illustrate the invention in the following Examples had acid contents in the latter range. For example, the acid content of the poly(n-butyl-acrylate-co-acrylic acid) (30:70 weight ratio) was 9.7 milliequivalents of acid per gram and the acid content of the poly(n-butyl acrylate-co-2-acrylamido-2-methylpropanesulfonic acid) (25:75 weight ratio) was 3.6 milliequivalents per gram.

The adhesive compositions of this invention also comprise, as essential ingredients, a substantially immobile, blocked photographic development restrainer, a substantially immobile, blocked competing photographic developer or mixtures of either or both.

Photographic development restrainers are known to be useful to restrain photographic development. The restrainers useful in this invention are "blocked", meaning they have a built-in blocking group which prevents activation of the restraining function before contact with the processing composition. The restrainers useful in this invention can have any suitable blocking group. Typically, when a blocked photographic development restrainer is subjected to an alkaline environment, such as an alkaline photographic processing composition, the blocking moieties are cleaved, providing activated photographic development restrainers.

The restrainers useful in this invention are also "substantially immobile", meaning they are immobilized to prevent their migration, to any appreciable extent, out of the mask adhesive into other layers such as image-recording layers prior to their activation. One conventional way of immobilizing the restrainer is to attach a ballasting group. In some restrainers, the blocking group can also serve as a ballasting group.

Any suitable substantially immobile, blocked photographic development restrainer can be used in practicing this invention, including those described in *Research Disclosure*, publication 15162, p. 84, Column 1, November, 1976 (published by Industrial Opportunities, Ltd., Homewell, Havant Hampshire, PO9 1EF, United Kingdom). Typical restrainers are those described in U.S. Patent 4,009,029 issued February 22, 1977. Such restrainers are represented by the formula (IV):

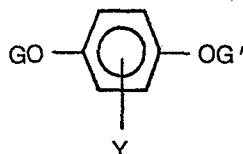


wherein R₁₃ is hydrogen, alkyl or substituted alkyl, typically of 1 to 8 carbon atoms, e.g. methyl, ethyl, chloromethyl, isopropyl or hexyl, aryl or substituted aryl typically of 6 to 12 carbon atoms, e.g. phenyl, xylyl or naphthyl; and Z comprises the nonmetallic atoms necessary to complete a 5- or 6-membered substituted or unsubstituted heterocyclic ring. These heterocyclic rings can be single rings as opposed to fused or condensed rings in which the atoms are members of more than one heterocyclic ring. Typical heterocyclic nitrogen moieties represented by formula (IV) include triazoles (e.g. 1,2,4-triazoles) benzimidazoles, pyrimidines, monoazoles (e.g. benzoxazoles or benzothiazoles) and tetrazoles. The substituents which can be present on the alkyl, aryl or 5- or 6-membered heterocyclic ring are subject to wide variation and naturally include those which are known to those skilled in the art (or can be easily determined by simple experimentation) to be substantially free of deleterious photographic effects. A detailed description of specific substituents is clearly not essential for an understanding of this inven-

tion. However, it appears appropriate to mention that such substituents can be hydrocarbon, for example, alkyl or aryl or they can be non-hydrocarbon such as halogen or alkoxy. Most preferably, the blocked development restrainers useful in this invention contain a tetrazole nucleus, such as a phenyl-substituted tetrazole nucleus. One such preferred substantially immobile, blocked development
5 restrainer is 5-(2-cyanoethylthio)-1-phenyltetrazole.

Competing photographic developers are well known in the photographic art to develop silver without causing dye release. Like the substantially immobile, blocked restrainers discussed herein-above, the competing photographic developers useful in this invention are both substantially "immobile" and "blocked". In this form, they will not migrate and will not be activated until contact
10 with the processing composition.

Any suitable substantially immobile, blocked competing developer can be used in this invention. Examples of suitable compounds are those described in U.S. Patent 4,201,578, issued May 6, 1980. Upon contact with an alkaline processing composition, the ester groups of these competing developers hydrolyze allowing the resulting hydroquinone to take part in development. The described competing
15 developers are represented by the formula (V):



wherein G is hydrogen, $-\text{COR}_{14}$ or $-\text{SO}_2\text{R}_{14}$, and preferably hydrogen; and G' is $-\text{COR}_{14}$ or $-\text{SO}_2\text{R}_{14}$, and preferably $-\text{COR}_{14}$. R_{14} is alkyl or substituted alkyl, typically of 1 to 20 carbon atoms, e.g. methyl, chloromethyl, ethyl, isopropyl, t-butyl, decyl or lauryl; aryl or substituted aryl, typically of 6 to 12 carbon
25 atoms, e.g. phenyl, xylyl or naphthyl as long as the compound can be hydrolyzed to the corresponding hydroquinone. Preferably, R_{14} is alkyl.

Y is hydrogen; alkyl or substituted alkyl, typically of 1 to 6 carbon atoms, e.g. methyl, ethyl, isopropyl or t-butyl; alkoxy or substituted alkoxy, typically of 1 to 6 carbon atoms, e.g. methoxy or ethoxy; aryl or substituted aryl, typically of 6 to 8 carbon atoms, e.g. phenyl, m-tolyl or p-methoxy-phenyl as long as the compound will diffuse at a sufficient rate when the acyl or sulfonyl group or
30 groups are hydrolyzed. Preferably, Y is alkyl. The substituents which can be present on the alkyl, alkoxy and aryl radicals in these competing developers are the same type as those present on the alkyl and aryl radicals in the development restrainers. Accordingly, specific substituents are those which do not cause
35 any significant deleterious photographic effects as exemplified by hydrocarbon radicals such as alkyl and aryl and non-hydrocarbon radicals such as halogen and alkoxy.

Useful substantially immobile, blocked competing photographic developers include hydroquinone diacetate, hydroquinone monohexanoate, hydroquinone monoacetate, t-butylhydroquinone monoacetate, hydroquinone monobenzoate, p-methylsulfonyloxyphenol, and p-tolylsulfonyloxyphenol.
40 A preferred compound is t-butylhydroquinone monoacetate.

The substantially immobile, blocked photographic developer is generally present in the adhesive compositions of this invention in a concentration in the range of from 2 to 20 percent, and preferably, from 5 to 10 percent, by weight based on total composition weight. In a dried adhesive layer of from 0.002 to
45 0.013 mm (0.1 to 0.5 mils) thick, the coverage of such blocked compounds is generally from 0.1 to 2 g/m^2 (10—200 mg/ft^2), and preferably from 0.15 to 0.75 g/m^2 (15—70 mg/ft^2), of surface area.

The adhesive compositions can also comprise various addenda commonly used in the art to enhance bond strength, improve coatability, prevent sticking of the coated material in roll form and provide surface texture and reflection properties. Typical addenda include dyes, pigments, fillers,
50 binders, polymer modifiers and waxes. Preferably, the compositions comprise silica, generally in an amount to provide coverage of from 0.2 to 0.7 g/m^2 (20—65 mg/ft^2) of surface area. Examples of suitable adhesive compositions include:

1. Poly(n-butyl acrylate-co-acrylic acid), 5-(2-cyanoethylthio)-1-phenyltetrazole and silica.
- 55 2. Poly(n-butyl acrylate-co-acrylic acid), poly(n-butyl acrylate-co-2-acrylamido-2-methylpropanesulfonic acid), 5-(2-cyanoethylthio)-1-phenyltetrazole and silica. The weight ratio of the carboxy-containing polymer to the sulfo-containing polymer in this composition is preferably in the range of from 50:50 to 70:30.
3. Poly(n-butyl acrylate-co-acrylic acid-co-2-acrylamido-2-methylpropanesulfonic acid), 5-(2-cyanoethylthio)-1-phenyltetrazole and silica.
- 60

The adhesive compositions described herein are formulated by any convenient method of mixing whereby an acidic polymeric component, a substantially immobile, blocked photographic development restrainer and/or a substantially immobile, blocked competing photographic developer and any other
65 desired addenda are mixed at ambient temperature in a suitable organic solvent (depending upon

boiling point) such as methanol or dimethylformamide, at from 10 to 40 percent solids. A specific technique for formulating an adhesive composition of this invention involves initially forming a solution of acidic polymer e.g., poly(n-butyl acrylate-co-acrylic acid) in methanol at ambient temperature. A separate solution of substantially immobile blocked development restrainer e.g. 5-(2-cyanoethylthio)-1-phenyltetrazole is then formed by placing the restrainer in a common solvent, heating for a few minutes at a temperature of approximately 120°C. to completely dissolve the restrainer and then cooling to ambient temperature. The two solutions are then combined using high agitation while adding silica to form the adhesive composition.

The adhesive compositions of this invention can be used in a wide variety of self-processing image-recording film units, and particularly in self-processing photographic film units. Typical formats of such film units are disclosed, for example, in U.S. Patents 2,543,181; 2,983,606; 3,362,819; 3,415,644; 3,415,646; 3,647,437; 3,635,707; 3,756,815; Canadian Patents 674,082 and 928,559; and *Research Disclosure*, publication 17643, paragraph XXIII, p. 30, December, 1978 (published by Industrial Opportunities, Ltd., Homewell, Havant Hampshire, PO9 1EF, United Kingdom). Preferred self-processing photographic products are of the type described in U.S. Patents 4,042,395 issued August 16, 1977, 4,061,496 issued December 6, 1977, and 4,190,447 issued February 26, 1980. A typical self-processing film unit has a photosensitive element, a cover sheet and a mask comprising an aperture adapted to receive the processing composition. The photosensitive element often comprises at least one image-recording layer and an image-receiving layer. The mask is bonded to the photosensitive element by the adhesive composition of this invention. Preferably, the film units comprise one or more radiation-sensitive, image-recording layers and associated dye-providing layers.

In addition, such film units can also contain other layers, e.g. neutralizing layers, timing layers, barrier layers, reflective layers, opaque layers, spacer layers, interlayers and the like. The film units can be treated with an alkaline processing composition to effect or initiate development. This processing composition can be supplied by external means or by an internal means, such as a container or rupturable pouch containing the processing composition, which is part of the film unit, as described, for example, in U.S. Patent 4,188,219 issued February 12, 1980. In addition, the film units can have means for collecting excess processing composition such as a trap element.

In general, the alkaline processing composition contains a developing agent, although the composition can also be simply an alkaline solution when the developing agent is elsewhere in the film unit. In the latter case, the alkaline solution activates the incorporated developing agent.

The image-recording elements of this invention do not necessarily contain an image-receiving layer. Such elements are not diffusion or image transfer film units. These elements can be used alone for recording and viewing an image or as part of a self-processing film unit. Typically, such an element comprises a support, a plurality of layers, including an image-recording layer, e.g., a photosensitive silver halide layer, and a mask. The adhesive composition of this invention is used to bond the mask to the image-recording layer or an intervening layer.

A detailed description of the components of the photographic products described hereinbefore and processes for using them are given in *Research Disclosure*, publication 15162, November, 1976 (published by Industrial Opportunities, Ltd., Homewell, Havant Hampshire, PO9 1EF, United Kingdom).

In bonding the mask to an appropriate layer in the elements and film units of this invention, the acidic adhesive composition can be coated in one or more layers to give the desired adhesive and photographic results. The acidic adhesive composition can be used to directly or indirectly bond the mask to the image-recording layer. For example, there may be intervening layers or other adhesives between the acidic adhesive composition and the mask or between the acidic adhesive composition and the image-recording layer. Within the meaning of this disclosure, such masks are permanently bonded to such image recording layers. As used herein "permanently bonded" means that the bonded layers and mask remain adhered together during ordinary usage. This is opposed to "temporary bonds" that allow layers to be peeled apart for usage.

The mask is sometimes made of a material, e.g. a polyester, such as poly(ethylene terephthalate), an organic-coated polymeric film or a laminate of a polymeric film, metal foil and paper, to which the acidic adhesive composition does not readily adhere. In such instances, it is advantageous to coat the mask with one or more "primers" or subbing layers which improve adhesion between the mask and the adhesive composition of this invention. Such priming is known and suitable primers include polyesters which can be coated out of organic solvents such as toluene, tetrahydrofuran, dioxane or chlorinated hydrocarbons.

A preferred primer for use in film units of this invention is a two-layer laminate. This laminate comprises a polyester, such as poly[ethylene-co-tetramethylene (72.5:27.5, molar ratio) azelate-co-terephthalate (47.5:52.5, molar ratio)], coated on the mask, and poly(ethylene-co-vinyl acetate) coated on the polyester. The adhesive composition of this invention is applied to the poly(ethylene-co-vinyl acetate).

Figures 1—3 illustrate a self-processing photographic film unit of the present invention. Referring to Figures 1 and 2, film unit 10 comprises support 12 which has a textured or glossy, substantially planar outer surface which forms the entire front or viewing surface of film unit 10. Support 12 is provided with an image-receiving layer 42, one or more reflective layers 44, one or more opaque layers

46 and one or more radiation-sensitive image-recording layers 14, e.g. photographic silver halide layers, to form photosensitive element 11 (see Figure 3). The visible image occupies the image area indicated by dashed rectangle 16. The border occupies the area outside dashed rectangle 16.

Covering film 19 is provided with one or more neutralizing layers 48 and one or more timing layers 50 to form cover sheet 18 (see Figure 3). Cover sheet 18 is arranged in superposition with and connected to support 12 with intermediate sheet 20 and spacer rails 30 and 32. Preferably, support 12 and cover sheet 18 are transparent to actinic radiation so that film unit 10 can be exposed to actinic radiation from the side illustrated in Figure 2 and viewed from the side illustrated in Figure 1.

Film unit 10 has a container or rupturable pouch 22 which can be of any suitable type known in the art. Pouch 22 carries a suitable alkaline processing composition capable of reacting with portions of radiation-sensitive, image-recording layer(s) 14 to produce a visible image. When appropriate pressure is applied to pouch 22, the processing composition is discharged and spread between image-recording layer(s) 14 and cover sheet 18 in a manner known in the art. At the end of film unit 10, opposite pouch 22, is trap element 24 having enough volume to receive and hold excess processing composition.

Intermediate sheet 20 is a unitary, multifunction sheet member which extends between and couples together support 12 and cover sheet 18. It also provides mask 26 which forms exposure aperture 28. Further, intermediate sheet 20 provides pouch attaching cover 34 and trap cover 36.

Mask 26 and spacer rails 30 and 32 provide requisite spacing between radiation-sensitive, image-recording layer(s) 14 and cover sheet 18 for the alkaline processing composition. Preferably, mask 26 and spacer rails 30 and 32 are opaque to actinic radiation. This opacity can be provided either with opacifying agents in the mask and spacer rails themselves or with an opaque layer coated thereon.

Referring to Figure 3, photosensitive element 11 comprises transparent support 12 which has thereon, in sequence, image-receiving layer 42, light reflecting layer 44, opaque layer 46 and radiation-sensitive, image-recording layer(s) 14. Mask 26 is bonded to element 11 with acidic adhesive 40. Primer layer(s) 38 provide(s) improved adhesion between mask 26 and acidic adhesive 40. Acidic adhesive 40 is open to exposure to alkaline processing composition when that composition is introduced into cavity 52 between layers 14 and 50. Spacer rail 32 is adhered to cover sheet 18 and mask 26 by any suitable adhesive (not shown) known in the art, such as a poly(ethylene-co-vinyl acetate)-based adhesive. Alternatively, cover sheet 18 can be self-adhering to spacer rail 32. Transparent cover sheet 18 comprises transparent covering film 19, which has thereon, in sequence, acid neutralizing layer 48 and timing layer(s) 50.

Evaluation of the bond strength of the adhesive compositions of this invention was made using the following procedure and equipment.

Preparation of peel samples

Poly(ethylene terephthalate) mask coated with the appropriate primer(s) and adhesive compositions of this invention, and various substrates to which the mask was to be bonded were cut into sample pieces 2.54x5.4 cm in size. Each mask sample was bonded to a substrate sample at one end to form a peel sample between two heated jaws at 138 kPa (20 psi) jaw pressure and various jaw temperatures for 0.4 second. The sealed area was 2.54x0.76 cm in size.

Post bond conditioning

Bonds were tested at different intervals after sealing to determine the effects of aging on the strength of the adhesive compositions.

In the "fresh" test, peel samples were placed in a 24°C/50% relative humidity environment for from 4 to 24 hours prior to peel tests under these conditions.

In the "one week natural aging" test, peel samples were placed in a 24°C/50% relative humidity environment for one week prior to peel tests under these conditions.

In the "four day, 49°C/10% RH" test, peel samples were placed in a 49°C/10% relative humidity environment for 4 days prior to peel tests at 24°C and 50% relative humidity.

In the "one day, 32°C/90% RH" test, peel samples were placed in a 32°C/90% relative humidity environment for at least 24 hours prior to peel tests under these conditions.

Peel tests

Peel tests of the samples were performed with a commercially-available Instron Tensile Tester (Instron Corp, of Canton, Mass., U.S.A.) in the following manner. Referring to Figure 4, the entire substrate 100 of a peel sample was adhered to a vertical mounting plate 102 on crosshead 104 with double adhesive pressure sensitive tape. The unsealed end of the mask 106 was opened away from substrate 100 by 180° and fixed in pneumatic jaws 108.

Crosshead 104 was then pulled downward away from jaws 108 at a rate of 25.4 cm/min. The force required to break the seal between mask 106 and substrate 100 was recorded.

The following examples illustrate the practice of the present invention.

Examples 1 and 2

Bond seal strengths of adhesive compositions

These examples illustrate the bond seal strengths of two adhesive compositions of this invention.

These compositions were used to bond a poly(ethylene terephthalate) mask to various substrates. The poly(ethylene terephthalate) mask was coated with two primer layers prior to being coated with the adhesive composition. The first primer layer was a coating of a polyester, poly[ethylene-*co*-tetramethylene (72.5:27.5, molar ratio) azelate-*co*-terephthalate (47.5:52.5, molar ratio)], and the second layer was a coating of a commercially available poly(ethylene-*co*-vinyl acetate)-based adhesive.

The adhesive composition of Example 1 comprised poly(n-butyl acrylate-*co*-2-acrylamido-2-methylpropanesulfonic acid) (25:75 weight ratio) (0.1 g), poly(n-butyl acrylate-*co*-acrylic acid) (30:70 weight ratio) (0.1 g) and 5-(2-cyanoethylthio)-1-phenyltetrazole (25 mg).

The adhesive composition of Example 2 was poly(n-butyl acrylate-*co*-2-acrylamido-2-methylpropanesulfonic acid) (25:75 weight ratio) (0.2 g) and 5-(2-cyanoethylthio)-1-phenyltetrazole (25 g).

Each adhesive composition was coated over the primer layers at a coverage of about 2.25 g/m².

The substrate materials listed in Table I were as follows: A=typical gelatin-containing silver halide emulsion layer of a photosensitive element of the type described in Example 2 of U.S. Patent 4,061,496 issued December 6, 1977; B=typical timing layer of poly(acrylonitrile-*co*-vinylidene chloride-*co*-acrylic acid); C=cellulose acetate film; and D=polystyrene film.

The conditions of sealing and the resulting fresh bond seal strengths are listed in Table I below. The data listed therein clearly illustrates that the adhesive compositions provided high strength permanent bonds (greater than 441 N/m (450 g/cm)) at several sealing temperatures when used to bond the primed mask to a gelatin-containing layer and a timing layer. The adhesive compositions did not effectively bond directly to cellulose acetate and polystyrene. However, the adhesive compositions form satisfactory bonds with the cellulose acetate and polystyrene films when appropriate adhesion promoting coatings are used.

TABLE I

Adhesive composition	Sealing temp. (°C)	Bond strengths (N/m)			
		A	B	C	D
Example 1	135	716	779	0	0
	149	724	794	9	0
	163	789	841	0	0
Example 2	135	866	820	0	0
	149	860	881	0	0
	163	843	906	0	0

Example 3

Bond seal strengths of adhesive composition

An adhesive composition of this invention was used to bond a primed mask of the type described in Examples 1 and 2 hereinbefore to a conventional gelatin-containing overcoat layer of a photosensitive element of the type described in Example 2 of U.S. Patent 4,061,496 issued December 6, 1977. The bond seal strength of this composition was then determined in the manner described in Examples 1 and 2 hereinbefore except that the coverage of acidic adhesive was 6.1 g/m².

The adhesive composition comprised poly(n-butyl acrylate-*co*-acrylic acid) (30:70 weight ratio) (5.6 g) and 5-(2-cyanoethylthio)-1-phenyltetrazole (490 mg). The conditions of sealing and the resulting bond seal strengths under various keeping conditions are listed in Table II hereinafter. The data from Table II illustrates that this adhesive composition has high bond strength under most conditions when sealed at conventional sealing temperatures. The bond strengths appear to increase with age and are advantageously high at high use temperature and humidity conditions.

TABLE II

Adhesive composition	Sealing temp. (°C)	Fresh	Bond sealing strength (N/m)		
			1 Week at 24°C, 50% R.H.*	4 Days at 49°C, 10% R.H.*	One day at 32°C, 90% R.H.*
Example 3	121	33	58	425	662
	135	505	560	812	664
	149	475	590	905	683

*Relative Humidity

Examples 4 and 5

Heat sealability comparisons

As previously indicated herein; in this invention the sulfo-containing polymers provide a significant decrease in heat sealing temperatures and improved heat sealing latitude in comparison to other acidic polymers. This advantage is illustrated by this example which is a comparison of three acidic components useful in this invention.

Each polymeric acid component was used to bond a primed mask of the type described in Examples 1 and 2 hereinbefore to a gelatin-containing overcoat layer of a photosensitive element of the type described in Example 2 of U.S. Patent 4,061,496 issued December 6, 1977. The bond seal strengths of each component were then determined in the manner described in Examples 1 and 2 hereinbefore except that the coverage of component was 6.1 g/m².

The component of Example 4 was poly(n-butyl acrylate-co-2-acrylamido-2-methylpropane-sulfonic acid) (25:75 weight ratio). The component of Example 5 was a 40:60 weight ratio mixture of poly(n-butyl acrylate-co-2-acrylamido-2-methylpropanesulfonic acid) (25:75 weight ratio) and poly-(n-butyl acrylate-co-acrylic acid) (30:70 weight ratio). A control component contained poly(n-butyl acrylate-co-acrylic acid) (30:70 weight ratio).

The conditions of sealing (seal temperatures) and the resulting bond seal strengths under various keeping conditions are listed in Table III hereinafter. The data from Table III show that the sulfo-containing polymers of Examples 4 and 5 which are useful in the adhesive compositions of this invention can be sealed over a broader range of sealing temperatures (and particularly at lower sealing temperatures) compared to the Control component while retaining their strength over most keeping conditions. As shown in Table III, adhesive strength was lost by Example 4 after prolonged exposure to extremely high humidity.

TABLE III

	Polymeric acidic component	Sealing temp. (°C)	Fresh	Bond sealing strength (N/m)		
				1 Week at 24°C, 50% R.H.*	4 Days at 49°C, 10% R.H.*	One day at 32°C, 90% R.H.*
30	Control	107	0	0	0	0
		121	0	22	88	466
		135	434	562	822	526
35		149	510	606	816	558
	Example 4	107	549	494	582	19
40		121	669	668	678	19
		135	670	660	641	22
		149	618	610	653	20
45	Example 5	107	33	218	414	565
		121	658	707	823	658
50		135	672	717	847	721
		149	691	729	873	748

*Relative Humidity

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Examples 6—13

Bond seal strengths and photographic effects of adhesive compositions

I. Bond seal strengths

Several adhesive compositions of this invention were used to bond a primed mask of the type described in Examples 1 and 2 hereinbefore to a gelatin-containing overcoat layer of a photosensitive element of the type described in Example 2 of U.S. Patent 4,061,496, issued December 6, 1977. The bond seal strengths of these compositions were determined in the manner described in Examples 1 and 2 hereinbefore except that the coverage of acidic adhesive was 6.1 g/m². For comparison purposes, a known adhesive composition comprising non-acidic poly-(ethylene-co-vinyl acetate) and designated Control A was similarly tested.

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The adhesive composition of Example 6 comprised poly(n-butyl acrylate-co-2-acrylamido-2-methyl propanesulfonic acid) (25:75 weight ratio) (5.2 g), 5-(2-cyanoethylthio)-1-phenyltetrazole (420 mg) and silica (520 mg). The composition of Example 7 was similar except the acidic polymer component was a 37.5:62.5 mixture (by weight) of poly(n-butyl acrylate-co-acrylic acid) (30:70 weight ratio), and poly(n-butyl acrylate-co-2-acrylamido-2-methylpropanesulfonic acid) (25:75 weight ratio). Examples 8, 9 and 10 were similar to Example 7 except that the polymer mixtures were present in 50:50, 62.5:37.5 and 60:40 weight ratios, respectively.

Examples 11—13 were similar to Example 6 except that poly(n-butyl acrylate-co-2-acrylamido-2-methylpropane sulfonic acid-co-acrylic acid) was used instead of the copolymer. These terpolymers were prepared from the appropriate monomers in weight ratios of 30:35:35, 30:31.5:38.5 and 30:28:42 for Examples 11—13, respectively.

The conditions of sealing and the resulting bond seal strengths under various keeping conditions are listed in Table IV below. All of the adhesive compositions, including the control provided high strength bonds over most keeping conditions. As shown in Table IV, adhesive strength was lost in Examples 6—8 after prolonged exposure to extremely high humidity.

TABLE IV

20	Adhesive composition	Sealing temp. (°C)	Fresh	1 Week at 24°C, 50% R.H.*	Bond sealing strength (N/m)	
					4 Days at 49°C, 10% R.H.*	One day at 32°C, 90% R.H.*
25	Control A	121	839	882	1112	618
		135	859	894	1041	564
		149	884	910	1154	597
30	Example 6	121	794	779	827	20
		135	785	782	843	11
		149	815	819	834	12
35	Example 7	121	513	530	816	263
		135	525	504	816	287
		149	535	499	790	270
40	Example 8	121	659	518	810	366
		135	647	570	824	370
		149	706	598	855	367
45	Example 9	121	546	541	913	753
		135	727	716	917	748
		149	843	725	936	726
50	Example 10	121	450	501	750	546
		135	631	677	797	613
		149	626	703	821	698
55	Example 11	121	1041	1038	1131	554
		135	1061	978	1141	565
		149	1076	1072	1119	549

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TABLE IV (cont.)

5	Adhesive composition	Sealing temp. (°C)	Fresh	1 Week at 24°C, 50% R.H.*	Bond sealing strength (N/m)	
					4 Days at 49°C, 10% R.H.*	One day at 32°C, 90% R.H.*
	Example 12	121	985	1089	1145	643
		135	988	1082	1161	641
10		149	988	1157	1153	633
	Example 13	121	1017	1094	1099	718
15		135	982	1069	1094	735
		149	968	1050	1084	735

*Relative Humidity

20 II. Photographic effects

Several diffusion transfer film units of the type described in Example 1 of U.S. Patent 4,061,496, issued December 6, 1977, were prepared. Several different adhesive compositions were used to bond a primed mask of the type described in Examples 1 and 2 hereinabove to the gelatin-containing overcoat (referenced layer 12 in that Example) of the photosensitive element. Each film unit was exposed to a test object and a processing composition was spread between the photosensitive element and the cover sheet by a pair of juxtaposed pressure rollers at either 16° or 22°C.

Some of the film units so exposed and processed were evaluated for border bleed. These film units were subjected to a 60°C/40% R.H. environment for 16 hours. The amount of border bleed was determined by measuring the increase in red, green and blue densities with a conventional densitometer in the normally white borders of the film units. The sensitometric data are listed in Table V below.

An evaluation of dark edge line is also presented in Table V.

In the data presented in Table V for dark edge line, an evaluation of 4 or less is good and means that very little of that defect was observed. An evaluation of 5 or 6 is fair, but acceptable in quality. An evaluation of greater than 6 is poor and indicates that dark edge line was so prominent that the image would likely be unacceptable to users.

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TABLE V

5	Adhesive	Border bleed (density increase)			Dark edge line	
		Red	Green	Blue	Processed at 22°C	Processed at 16°C
	Control A	0.131	0.075	0.095	—	6
	Example 6	0.070	0.043	0.053	—	3
10	Control B*	0.185	0.105	0.081	4	6
	Example 6a**	0.120	0.080	0.063	2	5
15	Control C*	0.164	0.071	0.063	5	8
	Example 6b**	0.101	0.061	0.063	2	4
	Example 10	0.124	0.079	0.068	3	6
20	Example 11	0.115	0.065	0.065	3	5
	Example 12	0.100	0.065	0.059	3	5
25	Control D*	0.176	0.100	0.078	5	8
	Example 6c**	0.096	0.064	0.060	3	5
30	Example 13	0.092	0.054	0.053	3	5

*Controls B—D were like Control A except the film units were from different coating runs.

**Examples 6a—6c were like Example 6 except the film units used were from different coating runs.

The data listed in Table V shows that the adhesive compositions of this invention, when used as mask adhesives in self-processing film units, greatly improve border quality in those film units. The improvement in border bleed is most prominently seen in the reduction of red density since most border bleed is attributable to undesired migration of cyan dye. That is, border bleed generally shows up as a cyan color in the border. Density increases in the green and blue regions of the spectrum are also reduced in most cases. The adhesive compositions of this invention also provide marked reduction in dark edge line over the control adhesives at both processing temperatures but especially at the lower processing temperature when dark edge line is usually more prominent. The film units of this invention were consistently evaluated as 6 or less, and many units were evaluated as 4 or less.

Considering the data presented in Tables IV and V together, it is apparent that the control mask adhesives provided high strength bonds, but were severely deficient in photographic properties (i.e. exhibited significant border defects). In contrast, the mask adhesives of this invention provide the needed high bond strengths while significantly reducing defects in the border.

Claims

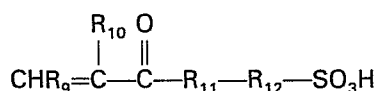
1. An image-recording element comprising:

- 1) a support,
- 2) a plurality of layers including an image-recording layer having an image area adapted to be processed by an alkaline processing composition, and
- 3) a mask providing an aperture adapted to reactive said alkaline processing composition and a border which defines said image area.

said mask being permanently bonded directly or indirectly to said image-recording layer by a high strength acidic adhesive composition which is disposed within said border and is subject to contact with said alkaline processing composition, characterized in that said adhesive composition comprises a polymeric acidic component that is adapted to neutralize said alkaline processing composition in said border and has at least 3 milliequivalents of acid per gram of said component, and a substantially immobile, blocked photographic development restrainer or a substantially immobile, blocked competing photographic developer.

2. An image-recording element according to Claim 1, characterized in that said polymeric acidic component comprises an acidic polymer having:

(a) from 5 to 90 percent, by weight, of units derived from a sulfo-containing monomer of the formula:



wherein each of R_9 , and R_{10} is hydrogen, methyl or halo; R_{11} is oxy or imino; and R_{12} is alkylene or arylene, and

(b) from 10 to 95 percent, by weight, of units derived from an additional polymerizable, ethylenically unsaturated monomer.

3. An image-recording element according to Claim 1, characterized in that said plurality of layers includes an image-receiving layer.

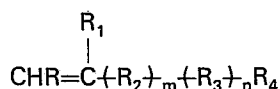
4. An image-recording element according to any of Claims 1, 2 or 3, characterized in that said image-recording layer is a radiation-sensitive image-recording layer.

5. An image-recording element according to Claim 4, characterized in that said element further comprises a rupturable pouch containing said alkaline processing composition.

6. A polymeric acid adhesive composition which is useful as a mask adhesive in an image-forming element of any of Claims 1—5, characterized in that said composition comprises a polymeric acidic component having at least 3 milliequivalents of acid per gram of said component, and a substantially immobile, blocked photographic development restrainer or a substantially immobile, blocked competing photographic developer.

7. An adhesive composition according to Claim 6, characterized in that said polymeric acidic component comprises an acidic polymer having:

(a) from 5 to 90 percent, by weight, of units derived from an acidic monomer of the formula:

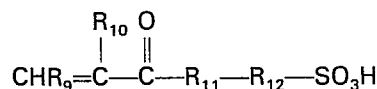


wherein each of m or n is 0 or 1; each of R and R_1 is hydrogen, methyl, halo or a monovalent acidic radical; R_2 is oxy, carbonyl, carboxyloxy or carbonylimino; R_3 is a divalent aliphatic, alicyclic or aromatic radical; and R_4 is a monovalent acid radical, alkyl or alkoxycarbonyl, provided that when R_4 is alkyl or alkoxycarbonyl, at least one of R and R_1 is a monovalent acid radical, and

(b) from 10 to 95 percent, by weight, of units derived from an additional polymerizable, ethylenically unsaturated monomer.

8. An adhesive composition according to Claim 6, characterized in that said polymeric acid component comprises an acidic polymer having:

(a) from 5 to 90 percent, by weight of units derived from a sulfo-containing monomer of the formula:

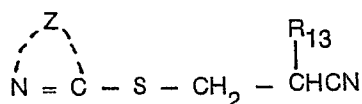


wherein each of R_9 and R_{10} is hydrogen, methyl or halo; R_{11} is oxy or imino and R_{12} is alkylene or arylene, and

(b) from 10 to 95 percent, by weight, of units derived from an additional polymerizable, ethylenically unsaturated monomer.

9. An adhesive composition according to Claim 8, characterized in that said polymeric acid component further includes a carboxy-containing linear addition polymer.

10. An adhesive composition according to Claim 6, characterized in that said substantially immobile, blocked photographic development restrainer has the formula:



wherein R_{13} is hydrogen, alkyl, substituted alkyl, aryl or substituted aryl; and Z comprises the non-metallic atoms necessary to complete a 5- or 6-membered substituted or unsubstituted heterocyclic ring.

11. An adhesive composition according to Claim 6, characterized in that said substantially
5 immobile, blocked competing photographic developer has the formula:



wherein G is hydrogen, $-\text{COR}_{14}$ or $-\text{SO}_2\text{R}_{14}$; G' is $-\text{COR}_{14}$ or $-\text{SO}_2\text{R}_{14}$ wherein R_{14} is alkyl, substituted alkyl, aryl or substituted aryl; and Y is hydrogen, alkyl or substituted alkyl, alkoxy or substituted
15 alkoxy, aryl or substituted aryl.

Revendications

1. Produit pour l'enregistrement des images comprenant

- 20
- 1) un support,
 - 2) un ensemble de couches comprenant une couche d'enregistrement de l'image ayant une plage d'image apte à être traitée par une composition de traitement alcaline, et
 - 3) un masque fournissant une ouverture apte à recevoir la dite composition de traitement alcaline et
25 une bordure qui définit la dite plage d'image,
- le dit masque étant fixé de façon permanente, directement ou indirectement, à la dite couche d'enregistrement de l'image, à l'aide d'une composition adhésive acide de force élevée qui est disposée au sein de la dite bordure et est apte à entrer en contact avec la dite composition de traitement alcaline,
- 30 caractérisé en ce que la dite composition adhésive comprend un constituant polymère acide qui est apte à neutraliser la dite composition de traitement alcaline dans la dite bordure et comprend au moins 3 milliéquivalents d'acide par gramme du dit constituant, et un retardateur de développement photographique bloqué, pratiquement immobile, ou un développeur photographique concurrent bloqué pratiquement immobile.

2. Produit pour l'enregistrement des images conforme à la revendication 1, caractérisé en ce que le dit constituant polymère acide comprend un polymère acide ayant:

a) de 5 à 90%, en masse, de motifs dérivés d'un monomère à groupe sulfo présentant la formule:



45 dans laquelle chacun des radicaux R_9 et R_{10} , est un atome d'hydrogène, un groupe méthyle ou un atome d'halogène, R_{11} est un groupe oxy ou imino et R_{12} est un groupe alkylène ou arylène, et,
b) de 10 à 95%, en masse, de motifs dérivés d'un monomère supplémentaire polymérisable, à insaturation éthylénique.

3. Produit pour l'enregistrement des images conforme à la revendication 1, caractérisé en ce que le dit ensemble de couches comprend une couche réceptrice d'image.

4. Produit pour l'enregistrement des images conforme à l'une quelconque des revendications 1, 2 ou 3, caractérisé en ce que la dite couche d'enregistrement de l'image est une couche d'enregistrement de l'image sensible au rayonnement.

5. Produit pour l'enregistrement des images conforme à la revendication 4, caractérisé en ce que le dit élément comprend, en outre, une capsule frangible contenant la dite composition de traitement alcaline.

6. Composition adhésive polymère acide, utile comme adhésif pour le masque d'un produit pour l'enregistrement des images conforme à l'une quelconque des revendications 1 à 5, caractérisée en ce que la dite composition comprend un constituant polymère acide contenant au moins 3 milliéquivalents d'acide par gramme du dit constituant, et un retardateur de développement photographique bloqué, pratiquement immobile.

7. Composition adhésive conforme à la revendication 6, caractérisée en ce que le dit constituant
65 polymère acide comprend un polymère acide contenant:

(a) de 5 à 90%, en masse, de motifs dérivés d'un monomère acide de formule:



dans laquelle m ou n sont chacun égaux à 0 ou 1; R et R₁ représentent chacun un atome d'hydrogène, un groupe méthyle, un atome d'halogène ou un radical acide monovalent; R₂ est un groupe oxy, carbonyle, carbonyloxy ou carbonylimino, R₃ est un radical divalent aliphatique, alicyclique ou aromatique et R₄ est un radical acide monovalent, un groupe alkyle ou alkoxy-carbonyle, l'un au moins des radicaux R et R₁ étant un radical acide monovalent lorsque R₄ est alkyle ou alkoxy-carbonyle, et, (b) de 10 à 95%, en masse, de motifs dérivés d'un monomère supplémentaire polymérisable, à insaturation éthylénique.

8. Composition adhésive conforme à la revendication 6, caractérisée en ce que le dit constituant polymère acide comprend un polymère acide contenant:

(a) de 5 à 90%, en masse, de motifs dérivés d'un monomère à groupe sulfo de formule:



dans laquelle R₉ et R₁₀ représentent chacun un atome d'hydrogène, un groupe méthyle ou un atome d'halogène; R₁₁ est un groupe oxy ou imino et R₁₂ est un groupe alkylène ou arylène, et, (b) de 10 à 95%, en masse, de motifs dérivés d'un monomère supplémentaire polymérisable, à insaturation éthylénique.

9. Composition adhésive conforme à la revendication 8, caractérisée en ce que le dit constituant polymère acide comprend, en outre, un polymère d'addition linéaire contenant des groupes carboxy.

10. Composition adhésive conforme à la revendication 6, caractérisée en ce que le retardateur de développement photographique bloqué, pratiquement immobile, présente la formule:



dans laquelle R₁₃ est un atome d'hydrogène, un groupe alkyle, alkyle substitué, aryle ou aryle substitué, et Z comprend les atomes non métalliques nécessaires pour compléter un noyau hétérocyclique à 5 ou 6 atomes, substitué ou non substitué.

11. Composition adhésive conforme à la revendication 6, caractérisée en ce que le dit développeur photographique concurrent bloqué, pratiquement immobile, présente la formule:



dans laquelle G est un atome d'hydrogène, un groupe —COR₁₄ ou —SO₂R₁₄; G' est un groupe —COR₁₄ ou SO₂R₁₄ dans lesquels R₁₄ est un groupe alkyl, alkyle substitué, aryle ou aryle substitué; et Y un atome d'hydrogène, un groupe alkyle ou alkyle substitué, alkoxy ou alkoxy substitué, aryle ou aryle substitué.

Patentansprüche

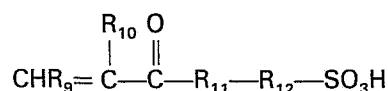
1. Bildaufzeichnungselement mit:

- 1) einem Schichtträger,
 - 2) einer Mehrzahl von Schichten einschließlich einer Bildaufzeichnungsschicht mit einem Bildbezirk, der mit einer alkalischen Entwicklungs-Zusammensetzung entwickelbar ist und
 - 3) einer Maske, die eine Öffnung für die Aufnahme der alkalischen Entwicklungs-Zusammensetzung und einen Rand, der den Bildbezirk definiert, bildet,
- wobei die Maske mittels eines sauren Klebers hoher Festigkeit, der im Bereich des Randes verteilt und dem Kontakt mit der alkalischen Entwicklungs-Zusammensetzung ausgesetzt ist, permanent direkt oder indirekt an die Bildaufzeichnungsschicht gebunden ist,

dadurch gekennzeichnet, daß der Kleber eine polymere saure Komponente, die derart beschaffen ist, daß sie die alkalische Entwicklungs-Zusammensetzung in dem Rand zu neutralisieren vermag und mindestens 3 Milliäquivalente Säure pro Gramm der Komponente aufweist und einen im wesentlichen immobilen, blockierten photographischen Entwicklungsverzögerer oder einen im wesentlichen immobilen, blockierten konkurrierenden photographischen Entwickler enthält.

2. Bildaufzeichnungselement nach Anspruch 1, dadurch gekennzeichnet, daß die polymere saure Komponente ein saures Polymer mit

(a) 5 bis 90 Gew.-% Einheiten, die sich von einem eine Sulfogruppe aufweisenden Monomer der Formel



ableiten, in der R_9 und R_{10} jeweils für ein Wasserstoffatom, eine Methylgruppe oder ein Halogenatom stehen; R_{11} eine Oxy- oder Iminogruppe ist und R_{12} eine Alkyl- oder Arylengruppe darstellt und (b) 10 bis 95 Gew.-% Einheiten, die sich von einem zusätzlichen polymerisierbaren ethylenisch ungesättigten Monomeren ableiten, enthält oder aus einem solchen besteht.

3. Bildaufzeichnungselement nach Anspruch 1, dadurch gekennzeichnet, daß zu der Mehrzahl der Schichten auch eine Bildempfangsschicht gehört.

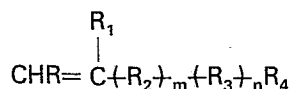
4. Bildaufzeichnungselement nach einem der Ansprüche 1, 2 oder 3, dadurch gekennzeichnet, daß die Bildaufzeichnungsschicht eine strahlungsempfindliche Bildaufzeichnungsschicht ist.

5. Bildaufzeichnungselement nach Anspruch 4, dadurch gekennzeichnet, daß das Element des weiteren eine aufspaltbare Tasche mit der alkalischen Entwicklungs-Zusammensetzung aufweist.

6. Polymerer Säure-Kleber, der als Masken-Klebstoff für ein ein Bild lieferndes Element nach einem der Ansprüche 1 bis 5 geeignet ist, dadurch gekennzeichnet, daß der Kleber eine polymere saure Komponente mit mindestens 3 Milliäquivalenten Säure pro Gramm der Komponente und einen im wesentlichen immobilen, blockierten photographischen Entwicklungs-Verzögerer oder einen im wesentlichen immobilen, blockierten konkurrierenden photographischen Entwickler enthält.

7. Kleber nach Anspruch 6, dadurch gekennzeichnet, daß die polymere saure Komponente ein saures Polymer mit:

(a) 5 bis 90 Gew.-% Einheiten, die sich von einem Monomer der Formel:

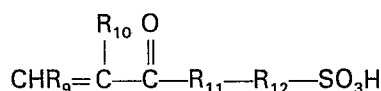


ableiten, worin bedeuten: m und n jeweils 0 oder 1, R und R_1 jeweils ein Wasserstoffatom, einen Methylrest, ein Halogenatom oder einen monovalenten sauren Rest; R_2 einen Oxy-, Carbonyl-, Carbonyloxy- oder Carbonyliminorest; R_3 einen divalenten aliphatischen, alicyclischen oder aromatischen Rest und R_4 einen monovalenten sauren Rest, einen Alkylrest oder einen Alkoxy-carbonylrest, wobei gilt, daß, wenn R_4 für einen Alkyl-, oder Alkoxy-carbonylrest steht, mindestens einer der Reste R und R_1 ein monovalenter Säurerest ist, und

(b) 10 bis 95 Gew.-% Einheiten, die sich von einem zusätzlichen polymerisierbaren ethylenisch ungesättigten Monomeren ableiten, enthält oder aus einem solchen besteht.

8. Kleber nach Anspruch 6, dadurch gekennzeichnet, daß die polymere Säure-Komponente ein saures Polymer mit:

(a) 5 bis 90 Gew.-% Einheiten, die sich aus einem eine Sulfogruppe aufweisenden Monomer der Formel:



ableiten, worin bedeuten: R_9 und R_{10} jeweils ein Wasserstoffatom, eine Methylgruppe oder ein Halogenatom; R_{11} eine Oxy- oder Iminogruppe und R_{12} eine Alkyl- oder Arylengruppe und

(b) 10 bis 95 Gew.-% Einheiten, die sich von einem zusätzlichen polymerisierbaren ethylenisch ungesättigten Monomer ableiten, enthält oder aus einem solchen besteht.

9. Kleber nach Anspruch 8, dadurch gekennzeichnet, daß die polymere Säure-Komponente des weiteren ein Carboxygruppen enthaltendes lineares Additionspolymer enthält.

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10. Kleber nach Anspruch 6, dadurch gekennzeichnet, daß der im wesentlichen immobile, blockierte photographische Entwicklungsverzögerer der folgenden Formel entspricht:



in der R_{13} für ein Wasserstoffatom, einen Alkyl-, substituierten Alkyl-, Aryl- oder substituierten Arylrest steht und Z die nicht-metallischen Atome darstellt, die zur Vervollständigung eines 5- oder 6-gliedrigen substituierten oder unsubstituierten heterocyclischen Ringes erforderlich sind.

10 11. Kleber nach Anspruch 6, dadurch gekennzeichnet, daß der im wesentlichen immobile, blockierte konkurrierende photographische Entwickler der folgenden Formel entspricht:



20 worin bedeuten: G ein Wasserstoffatom, $-\text{COR}_{14}$ oder $-\text{SO}_2\text{R}_{14}$; G' $-\text{COR}_{14}$ oder $-\text{SO}_2\text{R}_{14}$, wobei R_{14} ein Alkyl-, substituiertes Alkyl-, Aryl- oder substituiertes Arylrest ist und Y ein Wasserstoffatom, einen Alkyl-, substituierten Alkyl-, Alkoxy-, substituierten Alkoxy-, Aryl- oder substituierten Arylrest.

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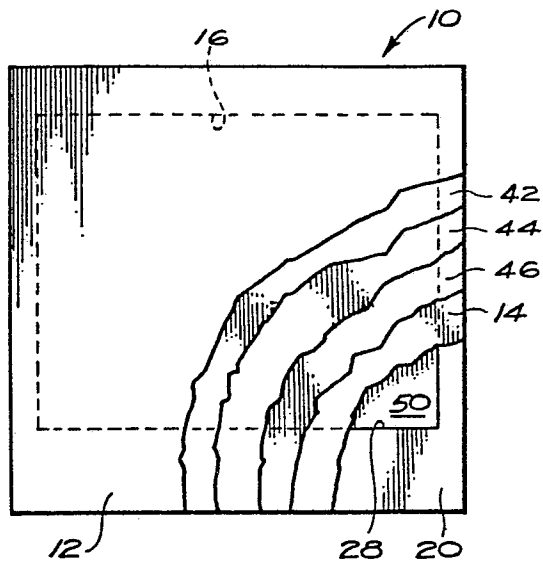


Fig. 1

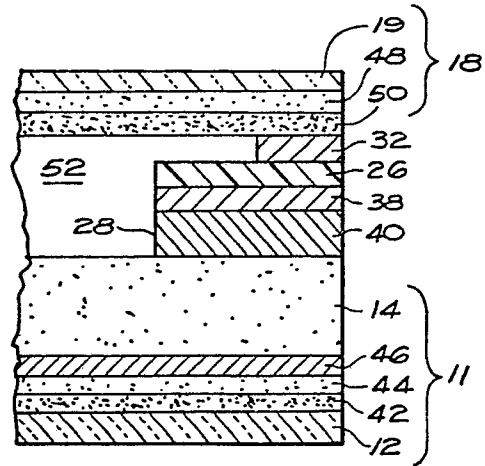


Fig. 3

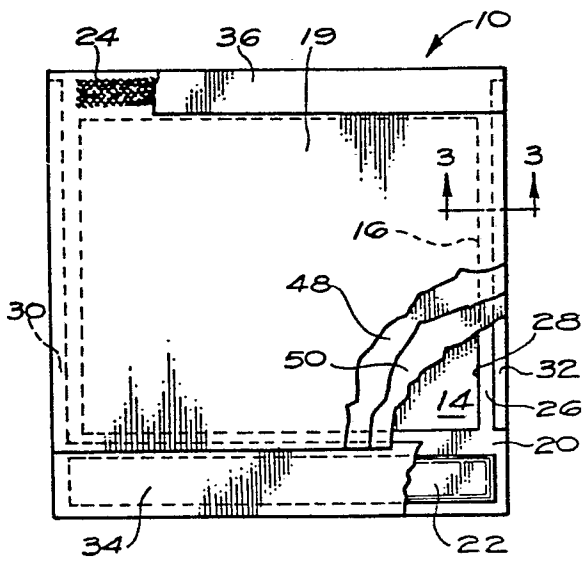


Fig. 2

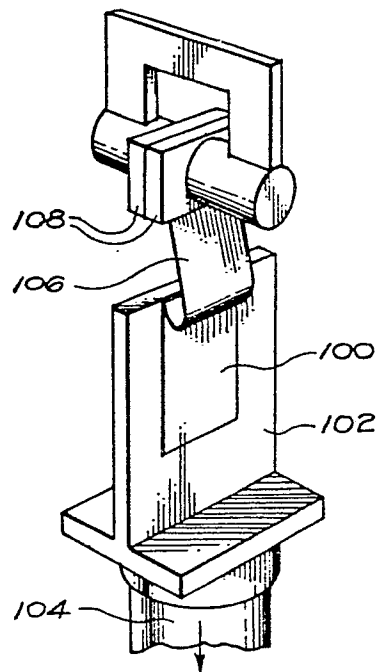


Fig. 4