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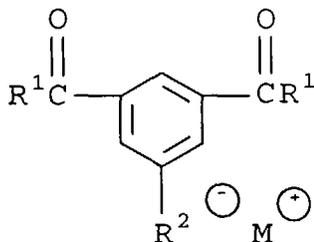
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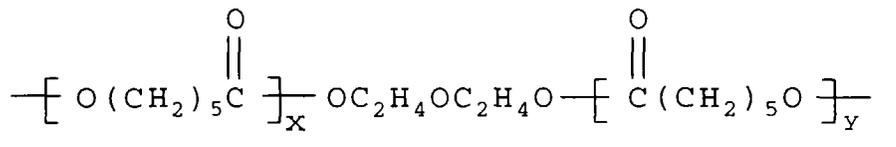
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(54) **Web cleaning roller and method of using same**

(57) A method of cleaning particles from a web by contacting the web with a web cleaning roller. The web cleaning roller (10) has a core (12) having thereon an exterior layer (14) of polyurethane. The polyurethane is copolymerized with a charge control agent of the formula



where R<sup>1</sup> represents:



R<sup>2</sup> represents sulfonate, oxyphenylene sulfonate, oxycyclohexylene sulfonate or p-toluenesulfonamidofonyl; x and y are integers which together are of sufficient value to achieve an R<sup>1</sup> molecular weight of 300 to 30,000; and M represents hydrogen, an alkali metal, ammonium or P<sup>+</sup>(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>CH<sub>3</sub>.

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The charge control agent is nonleachable from the polyurethane and is present in an amount sufficient to impart a selected amount of electric charge resistivity to the polyurethane. The durometer of the web cleaning roller is from about 15 to about 40 Shore A, and wherein said charge control agent prevents migration of moisture to said web during cleaning.

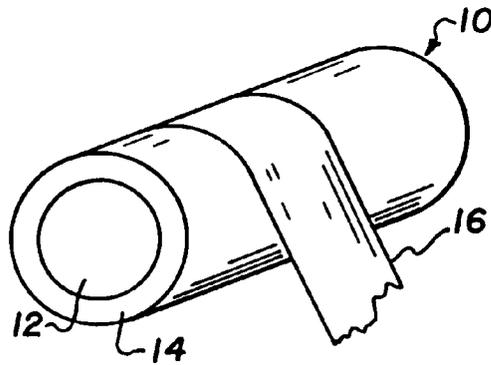


FIG. 1

**Description****Cross-Reference to Related Applications**

5 This application is a continuation-in-part of application Serial No. 08/285,607, entitled "Particle Transfer Roller and Method of Using Same", filed August 3, 1994, by Fernando Ramos and Paul Yacobucci.

**Field of the Invention**

10 This invention relates to a web cleaning roller comprising polyurethane copolymerized with a charge control agent. The invention also relates to a method of cleaning a moving web using the web cleaning roller.

**Background of the Invention**

15 Removal of particulate contamination from the surface of a web is important in many applications, such as cleaning exposed photographic film used in film projection systems, or in the manufacturing of photographic film and the like. Systems for removing particulate contamination from a web surface are well known. Examples of such systems include air knives and suction cleaning systems.

20 Web cleaning rollers that clean a web upon contact have proven to be particularly effective in removing particles from web surfaces. A web cleaning roller typically has an adhesive or tacky surface to which particles from the web surface adhere upon contact. A web cleaning roller having a tacky surface, such as a polyurethane roller having a Shore hardness in the range of 15 to 40, is often preferred over a web cleaning roller with an adhesive surface to avoid depositing adhesive on the web during cleaning.

25 A web, however, tends to accrue an electrostatic charge as it is conveyed over a roller, and the accrued charge tends to attract particulate contamination. Charge control agents can be added to a web cleaning roller during fabrication of the roller to inhibit the formation of the electrostatic charge. A problem with such charge control agents is that the charge control agents migrate to the surface of the web cleaning roller and can be deposited on the web being cleaned thereby contaminating the web. Another problem is that they are hygroscopic and can contaminate the web with moisture. Yet another problem is that they can be exhausted over a period of use, decreasing their effectiveness.

30 U.S. 4,729,925 discloses a copier transfer roller comprising polyurethane roller copolymerized with a nonleachable charge control agent capable of accepting an electrical bias for receiving and transferring toner. The disclosed copier transfer roller, however, is unacceptable for use as a web cleaning roller. The roller has a high durometer of from 40 to 90 Shore A such that the roller surface will not have a tendency to retain toner particles and therefore prevent transfer of toner from the roller surface to the paper. The opposite property is desirable in a web cleaning roller, where a lower durometer is desirable to obtain a good surface affinity for particle transfer to the roller surface and maintain a firm hold on the particles.

35 U.S. 4,762,941 discloses a transfer rollers used in electrophotographic equipment wherein charged particles, specifically complex developer materials, are accepted by the roller and then transferred from the roller to a media to produce an image. The web cleaning roller of this invention is designed to accept and retain from the web undesirable particles which effect product quality, such as contaminants like dust, lint etc.

40 It is an object of the invention to provide a web cleaning roller and method for its use having a nonleachable charge control agent therein. It is also an object of the invention to provide a web cleaning roller having an extended useable life.

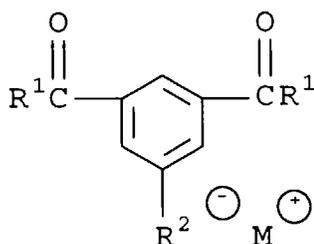
**Summary of the Invention**

45 It is, therefore, an object of the invention to provide a method of effectively cleaning a product web of particulate contaminants without leaving residual deposits on the product web.

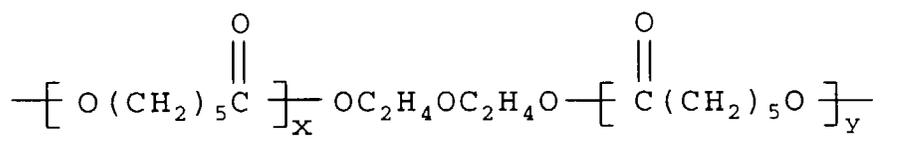
50 It is another object of the invention to provide a method of a product web with a charge control agent that does not impart moisture to the product web.

To accomplish these and other objects of the invention, a method is provided for cleaning a moving web, comprising contacting the web with a web cleaning roller having an exterior layer of polyurethane having a charge control agent copolymerized therein and having a Shore A hardness of from about 15 to about 40 durometers, and wherein the charge control agent has the formula

55



15 where R<sup>1</sup> represents:



25 R<sup>2</sup> represents sulfonate, oxyphenylene sulfonate, oxycyclohexylene sulfonate or p-toluenesulfonamidosulfonyl; x and y are integers which together are of sufficient value to achieve an R<sup>1</sup> molecular weight of 300 to 30,000; and M represents hydrogen, an alkali metal, ammonium or P<sup>+</sup>(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>CH<sub>3</sub>;

30 wherein the charge control agent is nonleachable from the polyurethane and is present in an amount sufficient to impart a selected amount of electric charge resistivity to the polyurethane; and wherein said charge control agent prevents migration of moisture to said web during cleaning.

The web cleaning roller of the invention, and method for its use, provide good charge control without the problem of leaching out of the charge control agent. The web cleaning roller does not contaminate the web being cleaned. The web cleaning roller effectively retains the charge control agent, extending its useful lifetime.

### 35 Brief Description of the Drawings

Figure 1 is an elevated view of a web cleaning roller of the invention in contact with a web.

40 Figure 2 is an elevated view of a web cleaning roller of the invention in contact with a web and having a backing roller at the region of contact.

Figure 3 is an elevated view of a web cleaning roller of the invention in contact with a film support and with charge measuring apparatus positioned as shown.

### 45 Description of the Preferred Embodiments

The web cleaning rollers of the invention are formed from polyurethane elastomers, using starting materials and methods that are well known in the art, and are copolymerized with a charge control agent further described below.

50 The polyurethane elastomers are formed by reacting polyisocyanate prepolymers, formed from an excess of an isocyanate, a hardener, and a plasticizer. The hardener comprises a polyol crosslinked and/or chain extended with at least one additional polyol. Prepolymers and hardeners useful in forming the web cleaning rollers of the invention are described in U.S. 4,762,941, incorporated herein by reference.

55 The plasticizer is added to control the hardness of the polyurethane elastomer in order to provide a resilient material useful in its intended environment as a web cleaning roller. Typically, a plasticizer such as a phthalate, for example, dibutyl terephthalate, provides good control over the hardness of the formed polyurethane article. Useful plasticizers also include adipates and glutarates and the like.

The charge control agent is a polyol that can be added to the polyol hardener in forming the polyurethane in an amount replacing a desired weight percentage of the hardener, as described in the Examples below. The nonleachable charge control agent should be present in an amount sufficient to impart the desired or selected amount of electric

charge resistivity to the formed polyurethane roller. Moreover, the preferred charge control agent should maintain a relatively constant electric resistivity over a wide range of relative humidity, particularly in low humidity environments, for instance from 10-30 % R.H. US Patent No. 941, hereby incorporated herein by reference, discloses the preferred charge control agent used in the web cleaning roller of the invention (structure shown below) having a relatively flat resistivity (<10X variability) response in a humidity range from about 10 to 75 % RH. The preferred charge control agent, therefore, meets this requirement in the web cleaning roller of the invention.

In a preferred embodiment, the charge control agent is present in the amount of from about 1 percent to about 8 percent by weight with the polyurethane. Most preferred is 4% by weight with the polyurethane.

Experience has taught that antistat and moisture on the product web result in objectionable defects in the product web, for instance, coating repellencies. Since antistats are hygroscopic, i.e., have the ability to readily absorb moisture from atmosphere, it is important to the invention that the preferred charge control agent not permit moisture to migrate to the surface of the web cleaning roller. Since the antistat of our invention does not migrate to the surface of the web cleaning roller, excess moisture is not attracted to the surface of the roller and thus can not be transferred to the web. Moreover, it is important that the antistat not transfer to the web since it also is a source of contamination on the product web.

FIG. 1 illustrates a web cleaning roller of the invention. Web cleaning roller 10 has a core 12 and an exterior polyurethane layer 14 over core 12's entire axially extending surface. Core 12 is made of rigid material such as stainless steel or aluminum. Layer 14 comprises polyurethane copolymerized with a charge control agent as described herein. Layer 14 is preferably applied to core 12 through a conventional casting process; however, it is also within the scope of the invention to cast layer 14 separately and then adhere or otherwise attach it to core 12. After layer 14 has been applied to core 12, conventional grinding techniques may be used to produce the desired finish and to obtain symmetry around the circumference of roller 10. The surface finish of layer 14 can in some applications be "as-cast", that is, without additional finishing steps carried out after casting the polyurethane in the roller mold. An as-cast coating 14 surface is generally sufficient for cleaning a web such as a photographic film and typically ranges from about 5 to 10 Ra,  $\mu$  IN (surface roughness, microinches). Other applications, such as when web 16 is paper, may require that the surface of coating 14 have additional finishing steps carried out to produce a less smooth finish, such as a satin surface finish of about 60 to 120 Ra.

Layer 14 need not be applied over the entire axially extending surface of core 12. Rather, layer 14 only need be applied to the area that will contact and clean the web in the intended use. Layer 14 has a Shore A hardness in the range of from about 10 to about 40 durometer, and a preferred hardness of about 25 durometer. A lower durometer coating is prone to accelerated wear and damage, especially in applications requiring a high web speed and/or acceleration. A higher durometer coating can result in leaving unacceptable marks and impressions on the web. Typically, these marks and impressions are caused by particles not compressing into the web cleaning roller. A preferred durometer for layer 14 is about 25. The thickness of layer 14 can depend on the intended application and factors such as the desired lifetime of roller 10, the web speed and acceleration, the anticipated rate of surface wear of roller 10, and the like. In one embodiment, layer 14 has a thickness in the range of 0.25 to 0.5 inch.

FIG. 1 shows roller 10 shown in contact with web 16 in a wrap mode configuration, that is, with web 16 wrapped around roller 10. A sufficient wrap tension should be provided to maintain web 16 in contact with roller 10 during cleaning as further described below. FIG. 2 illustrates an embodiment of the invention termed "positive contact mode" in which a backing roller 18 is provided to support the opposite side of web 16 at the region of contact of web 16 with roller 10. In this configuration, the wrap tension of web 16 against roller 10 can be lower than in the wrap mode shown in FIG. 1 since roller 10 and backing roller 18 provide a nip therebetween for maintaining sufficient contact force between web 16 and roller 10 at high web speeds, i.e., greater than about 100 feet per minute (fpm). Whether one employs a wrap mode or a contact mode, a web cleaning roller functions in a well known manner to remove particles from a web by contact with the moving web. The web cleaning roller has a larger coefficient of adhesion than that of the web, enabling the web cleaning roller to pull particles free of the web to accumulate on the surface of the web cleaning roller. The resiliency of the web cleaning roller is important for effective particle removal, as at durometers exceeding 40 Shore A, polyurethane roller 10 has a decreased capability for removing particles from web 16.

It is also important to the invention that web cleaning roller 10 have a high critical surface energy so that particulates which contact the surface will adhere to it. Critical surface energy (CSE) is a measure of the propensity of a particle or coating to adhere to a surface. CSE is expressed in terms of dynes/cm. It is known that the lower the CSE of a surface, the lower the adhesive strength between a particle or coating and the surface. Thus, if two surfaces are brought into contact with each other, contaminant particles, for instance lint, dust, etc, on either surface will be attracted to the surface with the higher critical surface energy. The CSE of web cleaning roller 10 is about 40 dynes/cm for the range of durometer hardness contemplated by the invention. A typical product web from which it is desirable to remove particulate contaminants during manufacturing has a CSE of about 32 dynes/cm. Thus, the web cleaning roller 10 of the invention with its much higher CSE will attract the particulate contaminants from the lower CSE product web, thus leaving the product web virtually free of objectionable particles on its surface.

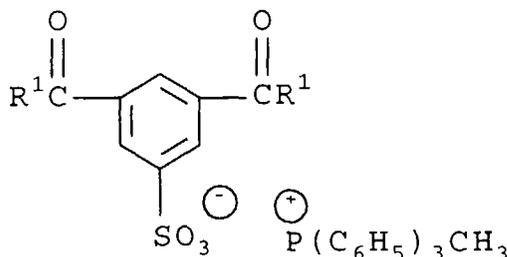
Another important characteristic of the particle adhesion ability of the web cleaning roller 10 of the invention is that it has a very low modulus of elasticity compared to a typical product web. The modulus of elasticity is the ratio of unit stress to unit strain within the proportional limit of a material in tension or compression. It is known that the lower the modulus of elasticity of a surface, the higher the adhesive force of the surface. Thus, if two surfaces are in contact with one another, the surface having the lower modulus of elasticity will attract particles from the surface having the higher modulus of elasticity. Kodak Estar™, a typical product web tested with the web cleaning roller 10 of our invention has a modulus of elasticity of about  $6.8 \times 10^6$  lbs/in<sup>2</sup>. Web cleaning roller 10 of the invention having a durometer of 25 Shore hardness has a modulus of elasticity of about  $150 \times 10^6$  lbs/in<sup>2</sup>. Hence, particulate contaminants on the product web when contacted by the web cleaning roller 10 will adhere to the web cleaning roller.

Web cleaning rollers can be made from any one of a number of commercially available polyurethane two-component mixes with a plasticizer additive and to which mixture a polyol charge control agent is added, such as NUCLEAR sold by Samuel Bingham Co., Conathane TU-4010, W-645 from Winfield Industries Inc., Buffalo, N.Y. and sold under the trade name Winthane, and LB22800 from American Roller Co. The following examples illustrate the preparation of a polyurethane web cleaning roller incorporating a charge control agent of the invention present in the described amounts.

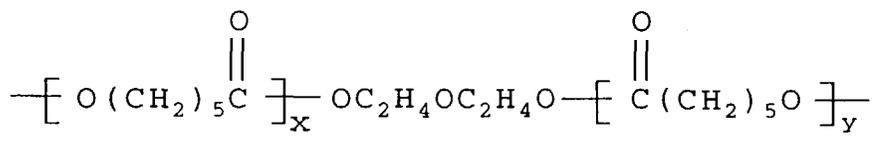
Examples 1 - 4

A two-component Conathane TU-4010 formulation comprising Parts A and B is used to form a polyurethane web cleaning roller of the invention. Part A is an isocyanate prepolymer and Part B is a polyol hardener. The charge control agent replaces a mole percentage of Part B. A third component, Part C, is a plasticizer such as dibutyl terephthalate which is provided for the purpose of lowering the durometer of the roller to a desired value.

The ingredients are weighed out directly into a mixing vessel as rapidly as possible. Part B is introduced into the vessel in an amount of 100 parts by weight decreased by the parts by weight of charge control agent added. A specified amount of a charge control agent, bis[oxydiethylenebis(polycaprolactone)yl]5-sulfo-1,3-benzenedicarboxylatetriphenylphosphonium salt (referred to hereinafter as "EK CCA"), is added to the vessel and the contents thoroughly stirred. The EK CCA has the structure represented by



where R<sup>1</sup> represents:



and where x and y are selected to provide a molecular weight for the R<sup>1</sup> group of about 530.

In Examples 1-4, 1 part, 2 parts, 3 parts, and 4 parts by weight of Kodak CCA, respectively, are added to 99, 98, 97, and 96 parts by weight, respectively, of Part B.

In each Example, Part C is then added to the vessel in an amount dependent on the desired durometer of the roller. The durometer can range from 40 Shore A when adding no amount of Part C to about 10 Shore A when adding about 0.6 parts of Part C per part of Part B by weight. Durometers of between 10 and 40 Shore A are obtained by mixing intermediate such ratios of Part C to Part B as described and recommended by the manufacturer. The contents of the vessel are then mixed.

Ten parts by weight of Part A are then introduced to the vessel and the resulting solution is well mixed. The solution is degassed under vacuum for 2 minutes at 28-29 inches of mercury after the collapse of the head. A steel core is cen-

trally positioned in a cylindrical mold and the solution poured into the mold. The mold is cured in an oven for 16 hours at 100 °C to form the casting. The mold and casting are cooled to room temperature after which the core with the casting thereon is removed and deflashed if necessary.

The electrical properties of the four rollers of the invention of Examples 1-4 are determined using the apparatus shown in FIG. 3. A film roll 100 holding a commercially available 35 mm photographic film 16A is positioned as shown. Film 16A is wrapped around polyurethane roller 10A. Roller 10A is allowed to freewheel against film 16A which is conveyed in the direction indicated at a speed of 1.0 m/s for all films tested, other than Kodacolor film which is conveyed at 3.5 m/s. The same tests are run, but using a web cleaning roller containing a conventional, commercially available charge control agent sold under the name Larostat present in the same weight proportions as the charge control agent of the invention. The surface charge for each run was measured and the results shown in Table I below.

TABLE I

EX:	Charge (nC/m <sup>2</sup> ):				
	Charge Control Agent	EASTMAN Color Negative	EKTAR 1000	Kodacolor	Vericolor
	1	EK CCA	1270	353	57
	Larostat	1130	433	30	665
2	EK CCA	344	304	24	275
	Larostat	281	208	53	258
3	EK CCA	160	218	29	218
	Larostat	194	276	64	124
4	EK CCA	79	276	25	261
	Larostat	147	200	75	134

The results demonstrate that the polyurethane rollers of the invention copolymerized with the non-leachable charge control agent exhibit a charge control capability comparable in to a polyurethane roller having a leachable charge control agent present in the same amounts.

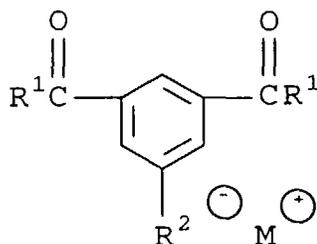
The web cleaning roller and method of the invention are useful in most web-cleaning applications, and particularly in those in which maintaining good particle cleaning efficiency is desired. The invention can therefore be employed in uses such as removing particulate contamination from exposed photographic film used in film projection systems, and in cleaning photographic film in preparation for or subsequent to applying emulsion layers thereon, to name but a few.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and the scope of the invention.

### Claims

1. A method of cleaning a moving web, comprising contacting the web with a web cleaning roller having an exterior layer of polyurethane having a charge control agent copolymerized therein and having a Shore A hardness of from about 15 to about 40 durometers, and wherein the charge control agent has the formula

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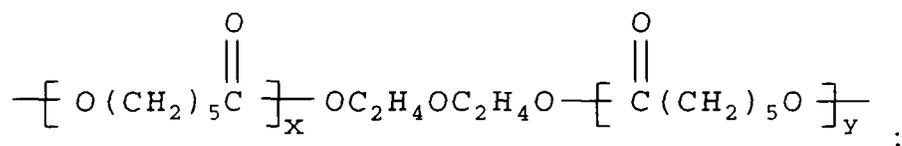


10

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where R<sup>1</sup> represents:

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R<sup>2</sup> represents sulfonate, oxyphenylene sulfonate, oxycyclohexylene sulfonate or p-toluenesulfonamidossulfonyl;

x and y are integers which together are of sufficient value to achieve an R<sup>1</sup> molecular weight of 300 to 30,000; and

M represents hydrogen, an alkali metal, ammonium or P<sup>+</sup>(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>CH<sub>3</sub>;

30

wherein the charge control agent is nonleachable from the polyurethane and is present in an amount sufficient to impart a selected amount of electric charge resistivity to the polyurethane; and wherein said charge control agent prevents migration of moisture to said web during cleaning.

35

2. The method of Claim 1, wherein the web is a photographic film.

3. The method of Claim 1, wherein the charge control agent is present in the amount of from about 1 percent to about 8 percent by weight with the polyurethane.

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4. The method of Claim 1, wherein the charge control agent is bis[oxydiethylenebis(polycaprolactone)yl]5-sulfo-1,3-benzenedicarboxylatetriphenylphosphonium salt.

5. The method of Claim 5, wherein the web cleaning roller has a Shore A hardness of 25.

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6. The method of Claim 1, wherein the polyurethane layer has a thickness in the range of 0.25 to 0.5 inch.

7. The method of Claim 6, wherein the polyurethane layer has a surface finish in the range of 5 to 10 Ra, μ IN.

8. The method of Claim 7, wherein the surface finish of the polyurethane layer is in the range of 60 to 120 Ra, μ IN.

50

9. The method of claim 1, wherein the exterior layer of the web cleaning roller has a critical surface energy of about 40 dynes/cm.

10. The method of claim 1, wherein the exterior layer of the web cleaning roller has a modulus of elasticity of about 150 x 10<sup>6</sup> lbs/in<sup>2</sup>.

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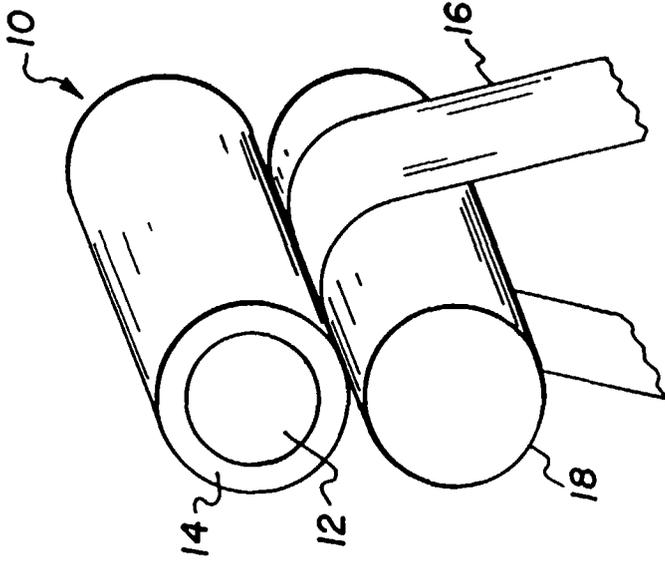


FIG. 2

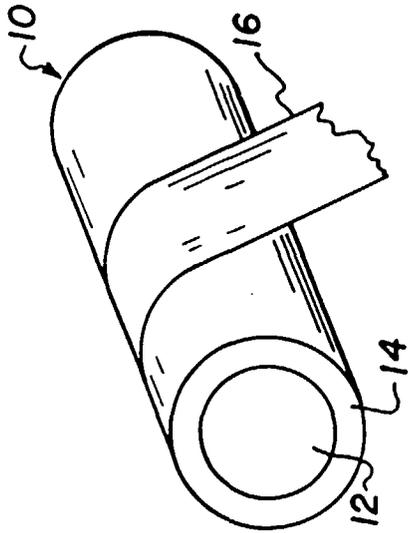


FIG. 1

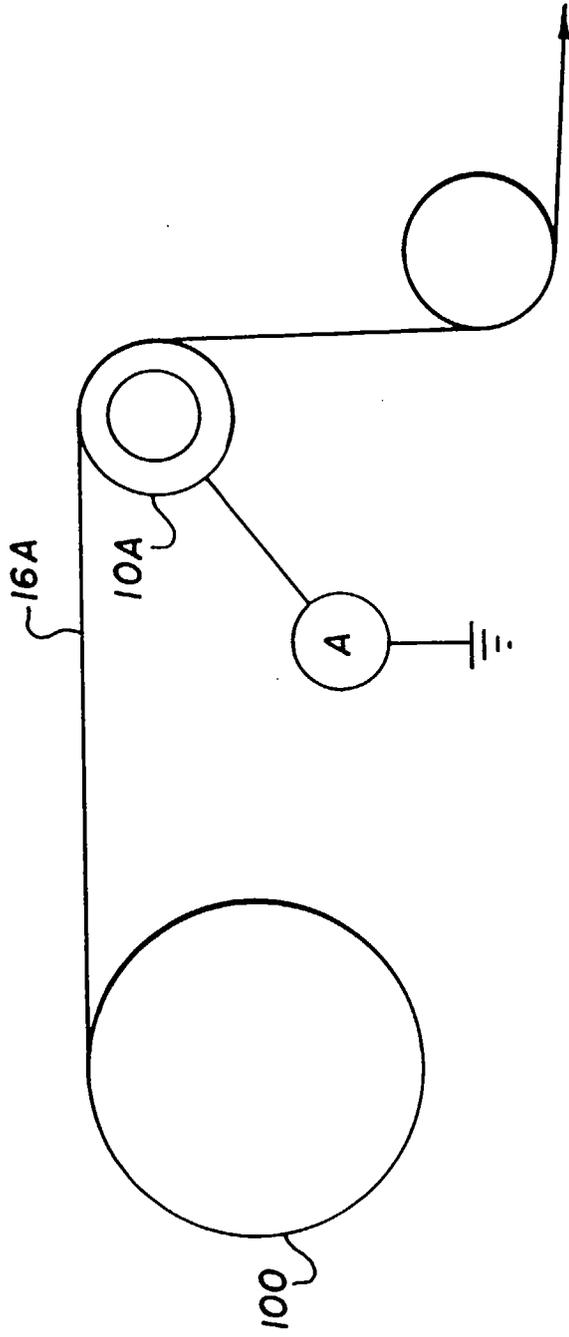


FIG. 3



European Patent  
Office

EUROPEAN SEARCH REPORT

Application Number  
EP 97 20 2535

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP 0 604 334 A (EASTMAN KODAK CO) * claims 1-10 * * page 4, line 29 - page 5, line 16 * ---	1-8	G03C11/06
D,A	US 4 729 925 A (T.J.CHENG ET AL.) * claims 1-7 * -----	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			G03C C08G
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		12 January 1998	Van Puymbroeck, M
CATEGORY OF CITED DOCUMENTS			
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