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[56] **References Cited**
UNITED STATES PATENTS
3,128,204 4/1964 Schavm et al. 117/221
FOREIGN PATENTS
680,310 2/1964 Canada 96/1

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[54] **AN ELECTROPHOTOGRAPHIC PROCESS AND ELEMENT EMPLOYING A CONDUCTIVE LAYER OF ETHERIFIED STARCH OR CELLULOSE**
7 Claims, 2 Drawing Figs.

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96/1R, 96/1.5, 204/18 PC
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B44c 1/04
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ABSTRACT: A process of visible image formation which comprises exposing a photoconductor layer having a high dark resistivity to electromagnetic radiation having a wavelength extending from the ultraviolet through the visible region said photoconductor layer being dispersed in electrically conducting contact with a layer comprising etherified starch or cellulose, as for example, hydroxyalkyl starch or alkoxy-cellulose, or unsymmetrical ethers of the form R-O-R₁ wherein R and R₁ are alkyl or aryl groups having at least one substituent which is of electron-withdrawing character.

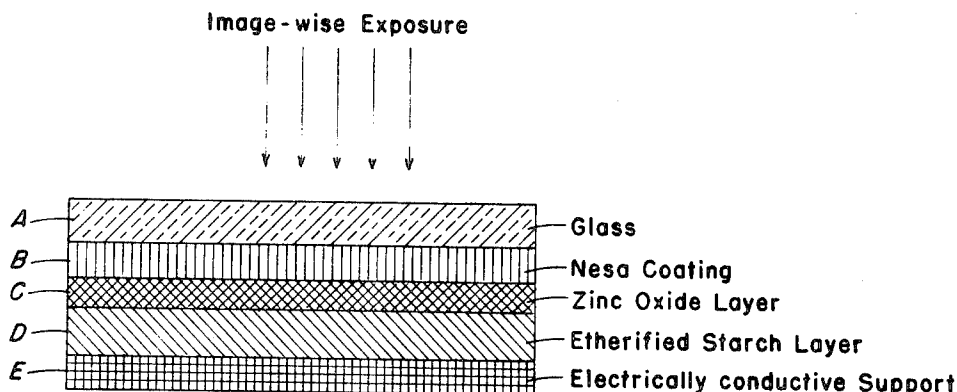


Fig. 1.

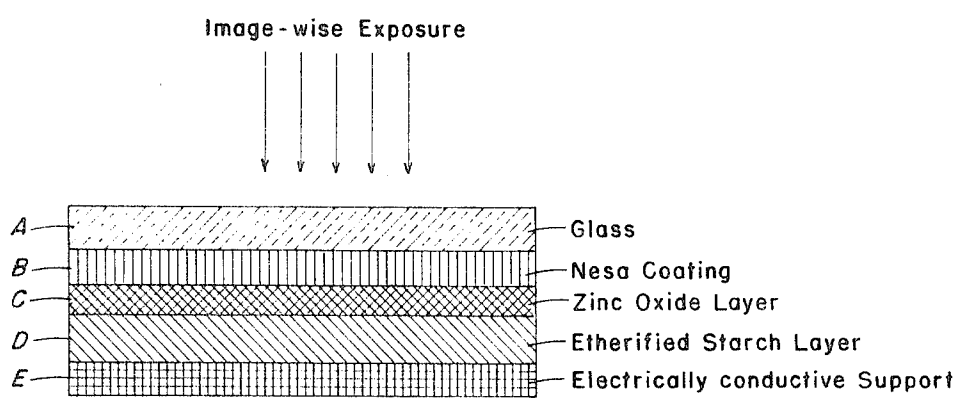
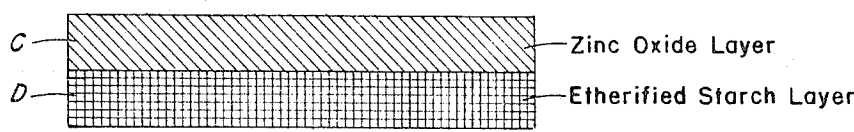


Fig. 2.

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AN ELECTROPHOTOGRAPHIC PROCESS AND ELEMENT EMPLOYING A CONDUCTIVE LAYER OF ETHERIFIED STARCH OR CELLULOSE

The present invention relates in general to photographic reproduction and in particular to the provision of an improved photoelectro method for the direct formation of a visible image.

Conventional methods of photographic reproduction for the formation of visible images, i.e., those which depend critically and directly upon the photolytic effects of actinic radiation for image reproduction, are found in many instances to be subject to one or more significant disadvantages. Thus, the effective photographic speed of such reproduction systems, apart from adjustments in the nature of the light-sensitive material employed, can be effectively enhanced according to but a relatively limited number of expedients including, for example, purposive adjustment of the radiant energy source itself (intensity) and/or increasing the duration of exposure (time). Such procedures, however, may well prove eminently unsatisfactory since the limitations and conditions necessarily imposed upon the type of processing equipment employed may become intolerable solely from an economic standpoint. In addition, the subject matter being reproduced, i.e., line-negative, drawing, etc. may be of such a nature as to militate against the propriety of employing extreme exposure levels. As will be readily evident, the effects of high-intensity exposure may deleteriously affect the photographic qualities of the negative material resulting in fading, loss of contrast, density, etc., thereby rendering such materials unsuitable for further photographic use. In the case of valuable documents, such conditions cannot be tolerated. Difficulties of the aforescribed type prove particularly problematical in connection with photographic reproduction techniques specifically adapted to yield a visible image directly upon exposure, absent any necessity for the utilization of a separate solution-developing operation. Processes of this type are generally referred to as "printout" as to be distinguished from "developing-out" methods, the latter invariably requiring some form of solution development treatment whereby to render visible the latent image deposits formed upon actinic exposure. Thus, in printout processing, the photolytic effects of the exposure radiation are manifested substantially immediately in the form of visible image deposits in accordance with the imagewise pattern of incident exposure radiation.

Printout processing has, of course, achieved preeminence in connection with office copying operations wherein speed of reproduction comprises all-important desiderata. However, effective implementation of this method of photoreproduction makes mandatory the use of high-intensity exposure levels which, for the reasons previously enumerated, may prove self-defeating and particularly, in those instances wherein it is imperative that any possibility of damage to the negative, positive, etc. being reproduced be virtually eliminated.

Moreover, of paramount significance from a commercial standpoint is the fact that the use of high-intensity radiant energy sources invariably leads to defective image reproduction as well as other deleterious effects. For example, high-intensity radiation sources of the type required in many of the printout methods currently known produce large quantities of infrared and heat rays which, as is well known, can exert catalytic effects and thus initiate as well as accelerate the image-forming reaction. As a consequence, a certain portion of the light-sensitive material may be exposed due to thermal effects alone which, of course, would tend to prohibit the production of a satisfactory image. For example, should a black and white silver halide negative pattern be employed, it is obvious that no image should form in areas corresponding to the dark portions of the negative pattern. However, such a result may nevertheless occur since the dark portions of the negative may well absorb significant amounts of the radiant heat energy given off by the light source to an extent sufficient to effect thermal exposure of the light-sensitive material. Consequently, in those systems which utilize a light source having

an appreciable radiant heat output, serious problems may arise in connection with the quality of the image reproduced.

In an effort to overcome or otherwise alleviate the foregoing and related problems, considerable industrial activity has centered around the research and development of image-forming systems capable of yielding high-quality reproduction and wherein any requirement for the use of inordinately high exposure levels is minimized if not completely obviated.

However, in the vast majority of instances, the innovations thus far evolved have provided only marginal advantage in such vital aspects as speed, image quality, etc., the latter shortcomings being particularly manifest in connection with photoreproduction techniques based upon the use of low energy radiation sources. For example, in an effort to extend as well as augment the spectral sensitivity of the light-sensitive materials heretofore promulgated, it has been suggested to incorporate therein one or more sensitizing dyes. Since these materials, being dyestuffs, are in many instances only partially absorptive in the visible spectrum, the light-sensitive composition will often be colored thereby. The consequences involved are self-evident. Furthermore, the increased costs involved in implementing such techniques have tended to retard any significant degree of commercial exploitation.

As a result of the discovery forming the basis of the present invention there is provided a completely novel method for effecting printout image reproduction wherein the effective photographic speed obtainable is virtually independent of the photolytic effects of actinic radiation. Thus, the problems implicit in reproduction processes which are essentially photochemical in nature, e.g., spectral sensitivity, exposure intensity, etc., are substantially irrelevant factors.

Accordingly, a primary object of the present invention resides in the provision of a method for the direct production of a visible image which is not subject to the above limitations and disadvantages.

Another object of the present invention resides in the provision of a high-speed method for forming a visible image directly upon exposure to actinic radiation wherein the exposure intervals required are reduced substantially. Another object of the present invention resides in the provision of a dry process for the direct formation of permanent images without any necessity for fixing or development steps.

A further object of the present invention resides in the provision of a method for forming a direct visible image wherein the image-forming reaction is totally independent of the direct photolytic effects of actinic radiation.

A still further object of the present invention resides in the provision of light-sensitive elements characterized by outstanding improvement in reproduction quality.

Other objects of the present invention will become apparent hereinafter as the description thereof proceeds.

The attainment of the foregoing and related objects is made possible in accordance with the present invention which in its broader aspects includes the provision of a process for direct formation of a visible image characterized in that image formation proceeds according to a reaction which is essentially electrolytic as distinguished from photolytic in nature, the activating influence being an electric current generated in accordance with a light pattern incident upon a photoconductive layer situated in electrically conducting contact with the image-forming layer.

The nexus of the present invention and that which represents the vital point of departure over printout methods totally dependent upon the photolytic effects of actinic radiation resides in the use of an image-forming layer comprising zinc oxide dispersed in a film-forming binder, said image-forming layer being in direct contact with a layer containing selected ether compounds as defined herein below, said zinc oxide under the effects of an electric current undergoing electrolysis resulting in the reduction of said zinc oxide to colored species. Accordingly, if an imagewise conductivity pattern be impressed upon such a layer, it will be readily evident that the zinc oxide reduction reaction generated in accordance

therewith will correspondingly determine the situs as well as extent of density buildup.

The method or process by which the present invention can be readily implemented can perhaps best be understood by reference to the accompanying drawing. However, it will be understood that the arrangement of parts depicted therein is given for purposes of illustration only and thus is in no way to be regarded as being limitative.

FIG. 1 illustrates one type of image-forming element applicable to the process of the present invention while FIG. 2 illustrates a fundamental arrangement by which the electrolytically induced image-forming reaction may be readily achieved.

In FIG. 1, C represents the image-forming layer comprising photoconductive zinc oxide dispersed in a resin binder and D represents the etherified layer. In FIG. 2, A represents a glass layer provided with a conductive coating B such as tin oxide and E represents a conductive support.

In actual operation, a DC voltage supply is connected across layers B (cathode) AND E (anode) thereby creating a substantially uniformly distributed electrical difference in potential across said anode and cathode layers. Without illumination, current of only a few microamperes, which would in any case be insufficient to initiate zinc oxide reduction, flows through the system due to the high dark resistivity of the zinc oxide layer. When exposed to a light pattern, however, an imagewise conductivity pattern is formed across the assemblage which causes a corresponding increase in the flow of current between the cathode and anode to an extent sufficient to initiate electrolytic reduction of the zinc oxide in layer C.

One of the truly outstanding features characterizing the process of the present invention relates to the fact that exceptionally high-speed image reproduction is readily obtainable notwithstanding the use of minimal exposure levels, i.e., exposure which would require the use of either ultra high-intensity radiation sources or conversely, intolerably protracted time intervals if image formation were to be effected to the same extent by utilizing corresponding photolytic methods. In contradistinction, the exposure required in practicing the present invention comprises but a fraction of those required in photolytic methods and need only be that necessary to render layer C conductive. Once the photoconductive zinc oxide layer is excited in accordance with the light pattern impressed thereupon, a copious source of current energy can be assured by merely controlling the density of the voltage impressed across the anode and cathode terminals. Since the image-forming electrolysis reaction in the zinc layer is a direct function of the number of coulombs impressed upon the system, means is thus provided for controlling the reduction rate and, concomitantly, the extent of density buildup virtually independently of the strength of the exposure radiation.

In photochemical methods, however, the exposure radiation performs a dual function, i.e., it provides both the information to be reproduced in the form of a light pattern and, in addition, represents both the ultimate and direct source of energy by which the image-forming reaction is initiated. In contradistinction, the function of the exposure illuminant in the present invention is solely to supply the information desired to be reproduced in visible image form, the direct energy source responsible for initiating the electrolytic reduction reaction being the electric current conducted by those portions of the photoconductive zinc oxide layer activated by the exposure radiation. In this respect, the use of electric energy to produce the reduction reaction constitutes an amplification function, i.e., the image to be reproduced, though optically sensed initially by the zinc oxide photoconductive layer, is converted to an amplified electric current. As will be readily apparent, this affords considerable latitude with regard to controlling the parameters which influence the zinc oxide reduction reaction rate.

As illustrated in the accompanying drawing, layer C comprises the zinc oxide photoconductor material dispersed in a suitable film-forming binder. It is preferred that the photocon-

ductive insulating layer possess a relatively high dark-resistivity, i.e., on the order of at least 10^{10} ohm-cm., and, of course, that it be easily rendered conductive when exposed to electromagnetic radiation having a visible wavelength ranging from the ultraviolet through the visible region of the spectrum. The zinc oxide material preferred for use in accordance with the present invention may be selected from any of those currently available commercially. However, particularly beneficial results are noted to obtain with the use of zinc oxide material available from the New Jersey Zinc Company under the trade name Florence Green Seal No. 8 and zinc oxide available from the St. Joseph Lead Company under the trade name St. Joe Zinc Oxide Grade 320-PC. As is well known, the zinc oxide normally employed in such photoconductive layers has its greatest sensitivity in the ultraviolet region of the spectrum whereas conventional light sources have relatively weak radiation in the same region. However, the sensitivity of the zinc oxide may be extended to the visible region of the spectrum by the incorporation of suitable sensitizing dyes capable of imparting response or sensitivity to the longer wavelength radiation.

The foregoing photoconductor materials are particularly preferred for use herein since they exhibit a peak spectral response substantially coextensive with that of the human eye, i.e., display a peak sensitivity to visible electromagnetic radiation, the response characteristics tapering off towards the ultraviolet and the infrared.

As examples of insulating binders found to be eminently suitable for the preparation of the photoconductive layer, mention may be made of the silicone resins such as DC-801, DC-804, and DC-996, manufactured by the Dow Corning Corporation, and SR-82, manufactured by the General Electric Corporation; acrylic and methacrylic ester polymers such as Acryloid A 10 and Acryloid B 72 supplied by the Rohm and Haas Company; epoxy ester resins such as Epidene 168, sold by the T. F. Washburn Corporation, etc.

As mentioned hereinbefore, a principal advantage made possible by the present invention relates to the manifold increase in speed obtainable by virtue of the fact that the incident exposure light energy is converted into electric energy and thereafter amplified to the extent desired in accordance with the particular speed requirements of the process. More specifically, the incident light is converted into charge carriers (current) by the photoconductor layer.

Any conductive support may be employed in accordance with the present invention, it only being necessary that electrical contact be established with the conductive surface during the exposure. Thus, for example, a carbon coating may be used on conventional film base supports. Metal, e.g., aluminum, may also be used as the conductive medium on which the zinc oxide or, alternatively, starch layer is coated. In addition, paper may be rendered electrically conductive by impregnation with carbon particles or by incorporation of suitable electrolytes at the time of manufacture. The support for the photoconductive coating may be glass or plastic on which is vacuum-evaporated or otherwise deposited a very thin film of metal or metal oxide such as electrically conducting glass commercially available and known as NESA glass. In the latter case, it is desirable that the metal layer be thin enough so that it is at least 70 percent to 75 percent transparent to light.

The thickness of the conductive support is likewise not particularly critical so long as the surface in contact with the zinc oxide or the etherified layer is suitably conductive. In general, it is found that optimum results can be obtained by selecting as the conductive base a material having a resistivity of less than 130 ohm-cm.

Another principal advantage made possible by the present invention relates to the direct reproduction of permanent images since the process of this invention is a dry one requiring neither a fixation nor a development step.

It has been found that this direct reproduction of permanent images can be achieved by the use of certain selected ether compounds which can be divided into two main groups. The

first of these is etherified starch or cellulose as exemplified by the hydroxyalkyl starches and the alkoxycelluloses. The second group encompasses the conventional ethers of the general formula

$R-O-R_1$ wherein R and R_1 represent alkyl or aryl such that the resulting ether can be either aliphatic, aromatic or mixed aliphatic/aromatic. In addition, the suitability of this latter group of ethers is enhanced by the presence of substituents which are electron-withdrawing. The compounds of both groups should, inter alia, have boiling points above 150° C., be compatible with other resins as needed in the formulation and, in the case of the starch derivatives, form solutions of said derivatives with a binding resin.

Any of the commercially available etherified starches and cellulose derivatives may be employed in the practice of the present invention in connection with the fabrication of layer D in the drawing. The parent starch material utilized for etherification is not particularly critical and may be selected from, for example, potato starch, wheat starch, rice starch, tapioca starch, and the like, the foregoing comprising but a partial enumeration of materials suitable for use. Moreover, the starch material may be provided in the form of the alkyl ether derivatives, e.g., methyl, ethyl, propyl, n-butyl, isobutyl, etc.; aryl, e.g., phenyl; aralkyl, e.g., benzyl, cumyl, etc. As specific examples of etherified starch found to be particularly suitable for use in the practice of the present invention, there may be mentioned without necessary limitation, the hydroxyalkyl starches which can be prepared by reaction of the appropriate alkylene oxide with starch solutions. A specific example is hydroxy propyl starch, an etherified starch material available commercially under the trade name designation Ceron N and manufactured by the Hercules Powder Corporation. Other acceptable materials of the etherified starch class include dinitrophenyl starch ether (dinitrophenoxystarch). In the etherified cellulose class are compounds such as methoxycellulose and ethoxycellulose.

The second group includes many commercially available ether compounds which are suitable for use in connection with the fabrication of layer D in the drawing. If the ether compound is a film former, layer D is prepared by direct application of a solution of the compound onto the conductive support followed by drying at room temperature. On the other hand, if the ether compound is not a film former, the layer is prepared by application of a solution of a suitable film former and the compound. In addition, the alkyl or aryl groups of these ethers may be substituted with electron-withdrawing groups preferably and with other groups if an electron-withdrawing group is also present. Examples of such compounds include:

- 2-bromo-4-hydroxyphenyl methyl ether (3-bromo-4-methoxyphenol)
- 3-carboxyphenyl methyl ether (m-methoxybenzoic acid)
- methyl carboxymethyl ether (methoxyacetic acid)
- di[sodium p-phenylsulfonate] ether (sodium diphenylether-disulfonate)
- sodium dodecyl diphenyl ether disulfonate

The system of imagewise electrocoloration, involving the reduction of zinc oxide which is in contact with a film containing an etherified material as described hereinabove can be achieved by another arrangement other than that previously

described. It consists of overcoating the zinc oxide coating with a solution containing the etherified material. If a transparent electrode is placed on the surface of the etherified coating, the system can be imaged through that coating. Such an arrangement would eliminate the need of the zinc oxide coating from being coated on a transparent electrode.

The following examples illustrate the invention in greater detail, although such examples are presented by way of illustration only, and are not to be construed as limiting the invention.

EXAMPLE 1

A dye sensitized zinc oxide photoconductive layer, approximately 50 microns thick was deposited on a sheet of NESA glass and allowed to dry in air overnight. The binder employed was GE Silicone Resin SR-82, and a mixture of toluene and methanol was used as solvent to adjust the mixture to the proper viscosity for coating.

Another coating was made on an aluminum sheet from an aqueous solution consisting of 40 percent Ceron N (etherified starch manufactured by the Hercules Powder Corporation) and 8 percent glycerine. That coating was also dried overnight at room temperature.

The two coatings were sandwiched together and 375-watt photoflood lamp was next positioned approximately 12 inches from the glass side of the photoconductive element. A 10-second exposure was made through a photographic continuous tone negative while simultaneously passing a current of 150 milliamperes at 250 volts through the assembly. The aluminum support was the anode and the NESA coated glass was the cathode. At the end of the exposure, a grey to black image was obtained on the surface of the zinc oxide coating at the interface of the two coatings.

EXAMPLE 2

On a zinc oxide photoconductive coating that was prepared by the procedure described in example 1, an aqueous solution containing Ceron N was coated on its surface.

A 375-watt photoflood lamp was placed 12 inches away and the arrangement was given a 10-second exposure through a photographic line negative while simultaneously applying a current of 60 milliamperes at a potential of 100 volts through the assembly. The photoexposure was made through the NESA coated glass which was placed on the surface of the Ceron coating. It was the anode, and the support for the zinc oxide coating was the cathode. At the end of the exposure, the image was reproduced.

EXAMPLES 3-6

These examples illustrate the suitability of other ether compounds, containing electron-withdrawing substituents thereon, as the materials in the etherified layer. The specific compounds and their coating solutions are tabulated below.

Example	Ether	Coating solution		
		Ether grams per 50 ml. of solvent	Glycerine ml. per 50 ml. of solvent	Solvent
3.	Sodium dodecyl diphenyl ether disulfonate.	3	2	20% aqueous gelatin solution.
4.	Dinitrophenoxystarch.	2.5	2	Water.
5.	Methoxyacetic acid.	5	2	20% polyvinyl alcohol.
6.	3-bromo-4-methoxyphenol.	3	2	20% aqueous gelatin solution.

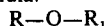
The above solutions were prepared, flow-coated onto thin aluminum sheets and air dried at room temperature. Zinc oxide photoconductive coatings on NESA glass sheets, prepared by the procedure described in example 1, were sand-

wiched to the etherified layers. In examples 3, 5, and 6, a 500-watt bulb having a color temperature of 2,870° K. was positioned 10 inches from the glass side of the photoconductive element and exposures of 30, 20 and 20 seconds, respectively, were made through a photographic continuous tone negative while simultaneously applying a potential of 100 volts. In example 4, a 375-watt photoflood lamp was positioned 12 inches from the glass side and an exposure of 10 seconds was made through the negative while simultaneously applying a potential of 200 volts. In all the examples, the aluminum support was the anode and the NESA coated glass was the cathode. At the end of the exposure, a grey to black image was obtained in each case on the surface of the zinc oxide coating at the interface of the two coatings.

The present invention has been disclosed with respect to certain preferred embodiments thereof, and there will be obvious to persons skilled in the art modifications, equivalents or variations thereof which are intended to be included within the spirit and scope of the invention.

What is claimed:

1. A process for the preparation of a visible image wherein image formation is controlled in accordance with an impressed, imagewise conductivity pattern which comprises imagewise exposing a photoconductor layer having a high dark resistivity and comprising zinc oxide dispersed in a film-forming binder to electromagnetic radiation having a wavelength extending from the ultraviolet through the visible region whereby said photoconductor layer is rendered capable of conducting electric current in the exposed areas, said photoconductor layer being disposed in electrically conducting contact with a layer comprising an etherified material and a conductive support wherein said etherified material is an ether of the general formula:



where R and R₁ are members selected from the class consisting of alkyl, substituted alkyl, monocyclic aryl, substituted monocyclic aryl, a starch radical and a cellulose radical such that when any one of R and R₁ is a member selected from the

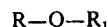
class consisting of a starch radical and a cellulose radical, the remaining moiety is a group other than starch and cellulose and such that, in the absence of a starch and cellulose group, at least one of R and R₁ contain a substituent which is of electron-withdrawing character and wherein an electrical potential difference is maintained across said photoconductor layer and said conductive support throughout the exposure interval, said potential difference being substantially uniformly distributed over said conductive support whereby current is caused to flow through said photoconductor layer, said exposure being carried out for a time sufficient to effect reduction of said zinc oxide.

2. A process according to claim 1 wherein said film-forming binder comprises a silicone resin.

3. A process according to claim 1 wherein said photoconductive support comprises an aluminum sheet.

4. A process according to claim 1 wherein said etherified material is hydroxypropyl starch.

5. An image-forming element comprising (1) a photoconductor layer comprising zinc oxide dispersed in a film-forming binder contiguous thereto, (2) an etherified layer comprising an ether of the general formula:



where R and R₁ are members selected from the class consisting of alkyl, substituted alkyl, monocyclic aryl, substituted monocyclic aryl, a starch radical and a cellulose radical, such that when any one of R and R₁ is a member selected from the class consisting of a starch radical and cellulose radical, the remaining moiety is a group other than starch and cellulose and such that, in the absence of a starch and cellulose group, at least one of R and R₁ contain a substituent which is of electron-withdrawing character, and (3) a conductive support.

6. An element according to claim 5 wherein said conductive support comprises aluminum.

7. An element according to claim 5 wherein said etherified layer comprises hydroxypropyl starch.

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