

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) Publication number:

**0 460 806 A2**

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: **91304006.9**

(51) Int. Cl.<sup>5</sup>: **G03G 5/05**

(22) Date of filing: **02.05.91**

(30) Priority: **06.06.90 JP 147578/90**

(43) Date of publication of application:  
**11.12.91 Bulletin 91/50**

(84) Designated Contracting States:  
**DE GB NL**

(71) Applicant: **Kinoshita, Koichi**  
**34-13, Nishi-Kusabuka-Cho**  
**Shizuoka-Shi Shizuoka-Ken(JP)**

(72) Inventor: **Kinoshita, Koichi**  
**34-13, Nishi-Kusabuka-Cho**  
**Shizuoka-Shi Shizuoka-Ken(JP)**

(74) Representative: **Enskat, Michael Antony Frank**  
**et al**  
**Saunders & Dolleymore 9, Rickmansworth**  
**Road**  
**Watford Hertfordshire WD1 7HE(GB)**

(54) **Electrophotographic sensitive member.**

(57) A photosensitive member for use in electrophotography comprises an electroconductive substrate and a photosensitive layer on top of the electroconductive substrate, the photosensitive layer comprising photoconductive fine particles dispersed in a self-hardening binder, and a liquid monomer impregnated into and hardened within the photosensitive layer. Preferably, the photoconductive fine particles comprise fine crystals of  $\alpha$ -type copper phthalocyanine and the liquid monomer is an instant adhesive, such as ethylcyanoacrylate.

**EP 0 460 806 A2**

The present invention relates to an electrophotographically sensitive member. More particularly, the present invention relates to an electrophotographically sensitive member which has a photosensitive layer comprising photoconductive fine crystals or particles dispersed in a thin layer of a self-hardening binder.

In patent application Ser. No. 260,683, filed October 20, 1988, now U.S. patent No. 4,963,452, which is incorporated herein by reference, the present inventor disclosed a photosensitive member having digital properties. This photosensitive member is characterized by a  $\gamma$  of the latent image formed thereon having a value of 6 or more. When this photosensitive member is charged to a high surface potential and illuminated with light, there is no observable change in the surface potential if the light intensity is below a predetermined threshold level. However, if the light intensity is above the threshold level, the photosensitive member suddenly discharges. In this respect, the photosensitive member described in U.S. 4,963,452 may be called digital.

The theoretical elucidation of the digital photosensitive member is based upon the triggering of an avalanche phenomenon when so-called intrinsic crystals having little crystal asymmetry or amorphous particles of a photoconductive material are dispersed in a highly insulative binder having a volume specific resistivity of at least  $10^{13} \Omega\text{-cm}$ . The use of intrinsic crystals or amorphous particles in combination with a highly insulative binder is considered necessary for triggering the avalanche phenomenon in a digital photosensitive member. This contrasts with prior art theories which tend to focus solely on the photoconductive material for determining the photosensitive properties of the member. The prior art theories regarding the binder are insufficient, and the interaction between the photoconductive particles and the binder has been insufficiently studied. Experimental efforts to improve the photosensitive characteristics of the member by making various changes in the binder have not been well thought out, and have been unable to give consistently good results.

The present invention focuses on problems associated with the binder, and has as its object to overcome these problems. More particularly, the present invention has as its object to overcome certain problems to be explained below which are associated with a self-hardening binder in a high  $\gamma$  photosensitive member used in a printer.

High  $\gamma$  photosensitive members are capable of printing with high resolution and high contrast. These properties are more useful in printers than in copiers where a certain degree of grey scale may be desired.

In electrophotographic printers as opposed to copiers, a so-called negative development process is used. This means that printing is achieved by blackening the parts of the photosensitive member that have received light input. This contrasts with a positive development process, often employed in copiers, where the areas that have not received light are blackened. The use of a negative development process creates certain major problems, especially when used with a digital photosensitive member, which are not encountered in a positive development process.

Photosensitive members used in printers up to now include those based on Se, hydrogenated amorphous silicon, and multilayer organic photoconductor systems wherein each layer performs a separate function. Up to now, there has been almost no use of binder-type photosensitive members in printers. The sole example known to the inventor of a binder-type photosensitive member in a printer employs a biased belt or roller to effect transfer. The inventor believes that this kind of transfer system is used in order to prevent damage to the surface of the photosensitive member which would occur if a transfer corona were used.

This arises from the fact that in printers using a negative development process, the polarity of the charging corona is the same as the charge polarity of the toner. Consequently, in order to effect transfer, a transfer corona would necessarily have a polarity which is opposite to the polarity of the charging corona. As is well known, a negatively charged corona produces more ozone than a positively charged corona, so that a negatively charged corona will lead to a more rapid deterioration of the photosensitive member. In a negative development process which employs both a charging corona and a transfer corona, one or the other of these coronas must of necessity be a negative corona. Because of this, it is important that an electrophotographically sensitive member which is used in a printer have durability in an ozone atmosphere. However, in binder-type photosensitive members which have photosensitive layers comprising fine particles of a photoconductive material set in a binder, there tends to be unevenness on the surface of the photosensitive layer and voids formed in the binder. This non-uniformity in the binder occurs during the hardening process. The non-uniformity of the binder thus tends to make binder-type photosensitive members more sensitive to ozone. Therefore, it is difficult to employ such photosensitive members in printers having transfer coronas.

In particular, in a printer employing a digital photosensitive member wherein the photosensitive layer is made from fine crystals of  $\alpha$ -type copper phthalocyanine dispersed in a self-hardening binder (as described in U.S. 4,963,452), the latent image retention properties of the member vary over a wide range depending

on whether or not transfer is effected by direct exposure to a corona. For example, if such a photosensitive member is used in a printer which employs a negative development process and a transfer corona, its capacity to retain a latent image drops with frequency of use and fog is seen in the background of printed pages.

5 It is therefore an object of the present invention to provide a photosensitive member for use in an electrophotographic printer which does not suffer from these deficiencies even when exposed to a conventional transfer corona. More particularly, it is an object of the present invention to provide a binder-type photosensitive member for use in an electrophotographic printer employing a negative development process which is resistant to ozone exposure and which exhibits excellent latent image retention capacity  
10 despite repeated use.

These and other objects are achieved by means of the present invention which provides a photosensitive member for use in an electrophotographic printer comprising an electroconductive substrate and a photosensitive layer on top of the electroconductive substrate, the photosensitive layer comprising photoconductive fine particles dispersed in a self-hardening binder material and a liquid monomer impregnated  
15 into and hardened within the photosensitive layer.

In a specific embodiment of the invention, a novel photosensitive member for use in an electrophotographic printer comprises an electroconductive substrate and a photosensitive layer on top of the electroconductive substrate, the photosensitive layer comprising fine particles of  $\alpha$ -type copper phthalocyanine dispersed in a self-hardening binder and a liquid instant adhesive, such as cyanoacrylate, impregnated into  
20 and allowed to harden within the photosensitive layer.

In a further aspect of the invention, a novel method for improving the latent image retention properties of a binder-type photosensitive member comprising a photosensitive layer of photoconductive fine particles dispersed in a self-hardening binder, comprises impregnating the photosensitive layer with a liquid monomer, such as cyanoacrylate, and allowing the liquid monomer to harden.

25 FIG 1 is a graph showing surface potential versus light input for a number of photosensitive members, including a photosensitive member in accordance with the present invention.

FIG 2 is a graph showing surface potential versus number of charge/discharge cycles for a number of photosensitive members, including a photosensitive member in accordance with the present invention.

In accordance with the present invention, a photosensitive member for use in electrophotographic  
30 printing which employs a negative development process is of the binder type and comprises an electroconductive substrate, such as aluminum, onto which a photosensitive layer has been applied. The photosensitive layer has a thickness of about  $5\mu\text{m}$  to about  $30\mu\text{m}$  and comprises fine particles of a photoconductive material dispersed in a self-hardening binder. The photoconductive fine particles preferably have a mean particle diameter of about  $0.01\mu\text{m}$  to about  $0.5\mu\text{m}$ . Preferably, the photoconductive particles are fine  
35 crystals of an intrinsic semiconductor or an amorphous semiconductor, and the binder has a volume specific resistivity of at least about  $10^{13} \Omega\text{-cm}$ , preferably about  $10^{15} \Omega\text{-cm}$ , whereby the photosensitive member has a  $\gamma$  of at least about 6 and has digital properties.

The photosensitive layer is impregnated with a liquid monomer that has been allowed to polymerize and harden by cross-linking. While not entirely understood, it is believed that the liquid monomer retards the deleterious effects of ozone by filling in the voids which are formed in the binder, thus improving the latent  
40 image retention capacity of the photosensitive member. Suitable liquid monomers are those known as instant adhesives, such as the alkyl cyanoacrylates. Among these methylcyanoacrylate, ethylcyanoacrylate, isobutylcyanoacrylate, isopropylcyanoacrylate, and  $\alpha$ -cyanoacrylic acid ethoxyethyl may be mentioned. These monomers are suitable because they have a low molecular weight and low viscosity, allowing them  
45 to impregnate the photosensitive layer without too much difficulty. Furthermore, they harden readily when exposed to even minute amounts of moisture. In fact, they harden so readily, in some cases the liquid monomer hardens on the surface of the photosensitive member before it has an opportunity to penetrate into the photosensitive layer. To overcome this, it is desirable to dilute the liquid monomer with a solvent, such as xylene, which slows the hardening process. As a result, the liquid monomer is able to fill the voids  
50 and repair the uneven surface of the binder, thus rendering binder-type photosensitive members more resistant to ozone exposure.

Other suitable liquid monomers which may be mentioned for the practice of this invention are acrylic urethane, silicone, and nitrocellulose.

An electrophotographically sensitive member of the present invention will now be explained with  
55 reference to the following examples.

#### Example 1

The following ingredients were finely mixed for three hours in a paint mixer (Model No. 5400-02 made by Red Devil Co.). The mixture was extracted to serve as the original composition for a photosensitive layer:

5	$\alpha$ -type copper phthalocyanine (made by Toyo Ink Seizo K.K.)	5.3 gr
10	polyester resin which is 60% solid and 40% solvent (Arumatekkusu P-645, (made by Mitsui Toatsu K.K.)	18.5 gr
15	melamine resin which is 70% solid and 30% solvent (Uban 20HS, made by Mitsui Toatsu K.K.)	6.7 gr
	cyclohexanone	95.7 gr
	ethanol	7.0 gr

20

Two aluminum cylinders 80mm in diameter, 288mm long and having a surface roughness of  $0.5\mu$  or less, were coated with a layer of soluble nylon (CM-8000 made by Toray K. K.) containing 10% by weight of  $I_2$  to a thickness of  $1\mu$ m on the surface and then dried. The nylon was coated by a process which is a variation of dipping. The purpose of this nylon/ $I_2$  layer is to provide an intermediate layer between the electroconductive substrate and the photosensitive layer.

Next, the previously prepared original composition was coated onto each of the two aluminum cylinders carrying the soluble nylon layer by the same coating method. After drying in air for about one hour, each of the aluminum cylinders was heated for three hours in an electric furnace at  $200^\circ\text{C}$ , and then cooled to obtain two untreated photosensitive members, each of which has a photosensitive layer about  $15\mu$ m thick. In general, the photosensitive layer may be between about  $5\mu$ m and about  $30\mu$ m thick, with the photoconductive fine particles having a diameter between about  $0.01\mu$ m and  $0.5\mu$ m dispersed in a self-hardening binder having a volume specific resistivity higher than  $10^{13} \Omega\text{-cm}$ .

One of the two untreated photosensitive members was then treated by coating with a liquid monomer, namely, an instant adhesive having ethylcyanoacrylate as its main ingredient (Aronarufua 101 made by Toa Gosei Kagaku K.K.) diluted with 50 wt% of xylene. Upon applying this liquid, the instant adhesive immediately permeates into the photosensitive layer. The photosensitive member initially shows luster which soon vanishes as the liquid permeates into the photosensitive layer. The treated photosensitive member was then exposed to warm air at  $80^\circ\text{C}$  for five minutes and was then cooled at room temperature for five minutes. This process was repeated four times until the photosensitive member retained its lustrous surface. For finishing, the treated photosensitive member was heated in an oven at  $100^\circ\text{C}$  for 10 minutes and then allowed to cool.

The treated photosensitive member (designated as A) and the untreated photosensitive member (designated as B) were installed in a printer that normally contains a commercial Se-type photosensitive member. This printer was not modified except that the developer unit was removed and the intensity of light in the erase lamp was increased 70-fold.

The developer unit was removed in order to speed up any deterioration caused by ozone. Normally, oxides formed on the surface of the photosensitive member by exposure to ozone adhere to the toner particles. These oxides are removed from the surface when the toner is removed. Thus, any damage caused by exposure to ozone occurs more rapidly if the developer unit has been removed.

Using this printer, the untreated photosensitive member A and the treated photosensitive member B were run through repeated cycles of (+ charging)  $\rightarrow$  (exposure to an image)  $\rightarrow$  (- charging) for as many as 10,000 cycles. The results are plotted in FIGS 1 and 2.

FIG 1 shows that initially both photosensitive members A and B display the same digital properties that are described in U.S. 4,963,452. However, after 700 cycles, untreated photosensitive member A shows a marked decrease in photosensitivity. After 3,000 cycles, photosensitive member A shows no photosensitivity at all. In contrast, the treated photosensitive member B continues to show substantially the same digital photosensitive properties even after 5,000 cycles.

FIG 2 is a graph showing the initial excitation surface potential that is obtainable after numerous cycles for photosensitive members A and B. FIG 2 also demonstrates the markedly superior properties of the treated photosensitive member B even after 10,000 cycles in comparison to the untreated photosensitive member A.

Although not entirely understood, the results shown in FIGs 1 and 2 may be explained in physical terms as follows. The ethylcyanoacrylate monomer present in the treating solution is an example of an instant adhesive. Compounds in this class are quickly volatilized by minute amounts of moisture and by cross-linked hardening. Other instant adhesives that perform in the same manner are methylcyanoacrylate, ethylcyanoacrylate, isobutylcyanoacrylate, isopropylcyanoacrylate and  $\alpha$ -cyanoacrylic acid ethoxyethyl. All of these materials have very low molecular weights because the acrylic monomer is their basic repeating unit.

Due to their low molecular weight, they have low viscosity and therefore superior coatability and permeability characteristics. They are therefore viewed as being effective for repairing incomplete coatings in binder-type photosensitive members wherein the photosensitive layer contains voids and has an uneven surface.

However, preliminary experiments have shown that a liquid containing only the monomer, when coated onto a photosensitive member and dried in a conventional atmosphere, such as at a temperature of 25 °C and a relative humidity of 60%, would not produce sufficiently good results. Thus, when a substantially pure solution of ethylcyanoacrylate monomer was coated onto the photosensitive member, it was observed that the liquid hardened very quickly and that a lustrous surface was formed on the photosensitive member which remained there. The so-treated photosensitive member showed almost no increase in charge retention properties despite several coatings being applied. At the same time, the photosensitivity of the member was decreased. It is believed that this was due to the almost instantaneous hardening of the liquid monomer, which did not permit it to permeate into the photosensitive layer.

In order to overcome this, the monomer solution was diluted with 50 wt% of xylene with the object being to control the extremely rapid hardening of the instant adhesive so that it would fully impregnate the photosensitive layer. Thus, it was found that a treatment solution containing ethylcyanoacrylate monomer as its main ingredient and 50 wt% of xylene in order to suppress the excessively rapid absorption and hardening of the instant adhesive molecules would not significantly alter the photosensitivity of the photosensitive member since it would permit the instant adhesive to permeate the photosensitive layer before hardening.

Xylene was chosen as the solvent since instant adhesives based on cyanoacrylate completely dissolve therein. Furthermore, since the molecular weight of the instant adhesive monomers is very low, there is almost no change in viscosity even under dilution with xylene, and permeation of the photosensitive layer occurs without hindrance. Even though diluted with xylene, the acrylic monomer will be absorbed into the photosensitive layer and absorption proceeds to completion as the xylene volatilizes. When xylene has finished volatilizing, there is absorption of moisture from the air, and the basic instant adhesive will harden into an acrylic resin. Once this is completed, it is possible to apply one or more additional coatings of the same treatment solution comprising liquid ethylcyanoacrylate monomer diluted with xylene. These additional coatings further improve the superior characteristics of the photosensitive member.

An important aspect of this invention is that the binder in the photosensitive layer is of a self-hardening type. This is important because self-hardening materials are characterized by a cross-linking reaction and the resulting material conventionally has very great resistance to solvents. Accordingly, there is no damage to the underlying structure of the photosensitive layer even when strong solvents are used as part of the treatment solution. Although xylene was chosen as the diluent, other substances can also be used. However, if a low boiling point solvent such as dichloroethane is used, the permeability of the treatment solution increases while the photosensitive layer is cooled because of rapid volatilization of the dichloroethane. This hinders absorption of moisture from the air during hardening of the acrylic monomer, and the acrylic layer tends to be incomplete. This problem can be eliminated if the photosensitive member is maintained at a temperature about 20 to 30 °C above ambient during the coating process when a diluent such as dichloroethane is used.

While the treatment solution used in this example contained ethylcyanoacrylate as its main ingredient, other acrylic monomers may also comprise the main ingredient of the treatment solution. An instant adhesive whose main ingredient is ethylcyanoacrylate monomer has high permeability and is very easy to use from the standpoint of coatability. These same properties may be found in other monomeric materials, for example, in urethane modified silicone. However, it is necessary to ensure that the liquid monomer that is used is sufficiently permeable in the photosensitive layer so that it may penetrate therein. Problems in permeability may be overcome to a certain extent by applying the coating under an overpressure so as to

force permeation to occur. Alternatively, the monomeric material may be impregnated into the internal structure of the photosensitive layer by first coating the photosensitive layer with a monomeric solution of low viscosity, followed by coating with a second monomeric solution of higher viscosity, and, if necessary, by coating the photosensitive layer with a third monomeric solution of yet higher viscosity.

5

## Example 2

Three treatment solutions containing the following monomers and solvent were prepared:

1. Urethane modified silicone 3% + ethyl acetate;
- 10 2. Urethane modified silicone 9% + ethyl acetate; and
3. Urethane modified silicone 15% + ethyl acetate.

An untreated photosensitive body was prepared in the same manner as described in Example 1. The untreated photosensitive body was coated sequentially with each of the three monomeric solutions described above and dried to give photosensitive member C. The photosensitive member C had a mirror  
15 surface luster. The photosensitive member C was then tested for photosensitive properties in the same manner as described in Example 1.

The results are plotted on FIGs 1 and 2. As shown, although not as good as photosensitive member B, photosensitive member C was a clear improvement over the untreated photosensitive member A. Furthermore, the method of this example in which liquid monomers of different viscosities are used can be adapted  
20 for many different monomeric materials. Among these are acrylic urethane, silicone and nitrocellulose.

The technology of the present invention can also be taken into account in matching the toner to the properties of the photosensitive member. As is well known, a high degree of matchability is required between the photosensitive member and the toner and carrier. Once the characteristics of the photosensitive member are selected, there is little freedom allowed for choosing the characteristics of the toner and  
25 carrier with a high degree of matchability.

Knowledge regarding toner and carrier properties which was obtained in prior copier technology was based upon the premise that the charge on the toner and the photosensitive member are opposite in polarity. On the other hand, in a printer which employs a negative development process, the charge on the toner and the photosensitive member are the same polarity. Because of this, combinations of toner and  
30 carriers that are good for prior copying systems may not necessarily be good for printing systems. What is important, however, is the ability to select a photosensitive member having different work functions. With prior known binder-type photosensitive members, it is extremely difficult to control the work function of the photosensitive member by stabilizing the photoconductive properties.

In this regard, the fact that many different monomeric materials can be used to impregnate the photosensitive member and that very little variation in photoconductive properties are thereafter observed, as explained in Example 2, means that as a consequence the range over which the work function can be  
35 varied is also very large.

## Example 3

40

In this example, Examples 1 and 2 were combined. A photosensitive member similar to photosensitive member B was prepared using ethylcyanoacrylate monomer as the main ingredient for impregnation except that the number of coatings was increased three-fold. Thereafter, a mixed solution of urethane modified silicone 8% + ethyl acetate was applied as a final coating and the photosensitive member was dried to  
45 complete its manufacture.

This photosensitive member was then tested in the same manner as in Examples 1 and 2. This so-treated photosensitive member showed nearly the same photoconductive properties including latent image retention properties, as the photosensitive member B of Example 1.

The same results were obtained when using other kinds of monomers as the final coating step, for  
50 example, acrylic urethane silicone. As long as sufficient care was taken to select a final coating which had a high resistance, it was found that the durability of the photosensitive member was maintained and that the work function properties of the surface could be varied.

Thus, a photosensitive member which has a photosensitive layer comprising photoconductive fine particles dispersed in a self-hardening binder can be improved by being impregnated with a monomeric  
55 material. The monomeric material hardens and fills the voids and other defects in the photosensitive layer, thereby increasing the latent image retention properties of the photosensitive member.

While the invention has been described by reference to specific examples, this was for purposes of illustration only. Numerous alternative embodiments will be apparent to those skilled in the art.

## Claims

1. A photosensitive member for use in electrophotography, comprising  
an electroconductive substrate, and  
5 a photosensitive layer on top of said electroconductive substrate, said photosensitive layer comprising photoconductive fine particles dispersed in a self-hardening binder, and a liquid monomer impregnated into and hardened within said photosensitive layer.
2. A method for improving the latent image retention properties of a binder-type photosensitive member comprising a photosensitive layer of photoconductive fine particles dispersed in a self-hardening binder,  
10 said method comprising  
impregnating said photosensitive layer with a liquid monomer, and  
causing said monomer to harden.
- 15 3. The member of Claim 1 or method of Claim 2, wherein said liquid monomer is an instant adhesive.
4. The member of Claim 1 or method of Claim 2, wherein said liquid monomer is an alkylcyanoacrylate.
5. The member of Claim 1 or method of Claim 2, wherein said liquid monomer is methylcyanoacrylate, ethylcyanoacrylate, isobutylcyanoacrylate, isopropylcyanoacrylate or  $\alpha$ -cyanoacrylic acid ethoxyethyl.  
20 6. The member of Claim 1 or method of Claim 2, wherein said liquid monomer is urethane modified silicone, acrylic urethane, silicone or nitrocellulose.
- 25 7. The member of Claim 1 or method of Claim 2, wherein said photoconductive fine particles comprise fine crystals of an intrinsic semiconductor or an amorphous material, and said binder has a volume specific resistivity of at least about  $10^{13} \Omega\text{-cm}$ .
8. The member or method of Claim 6, wherein said photoconductive fine particles comprise fine crystals of  $\alpha$ -type copper phthalocyanine.  
30 9. A photosensitive member for use in electrophotography, comprising  
an electroconductive substrate, and  
a photosensitive layer on top of said electroconductive substrate, said photosensitive layer  
35 comprising fine crystals of  $\alpha$ -type copper phthalocyanine dispersed in a self-hardening binder, and a liquid cyanoacrylate impregnated and hardened within said photosensitive layer.
10. The photosensitive member of Claim 9, wherein said cyanoacrylate is ethylcyanoacrylate.
- 40 11. The photosensitive member of Claim 9, wherein said liquid cyanoacrylate is diluted with an inert solvent.
12. The photosensitive member of Claim 9, wherein said binder has a volume specific resistivity of at least about  $10^{13} \Omega\text{-cm}$ .

45

50

55

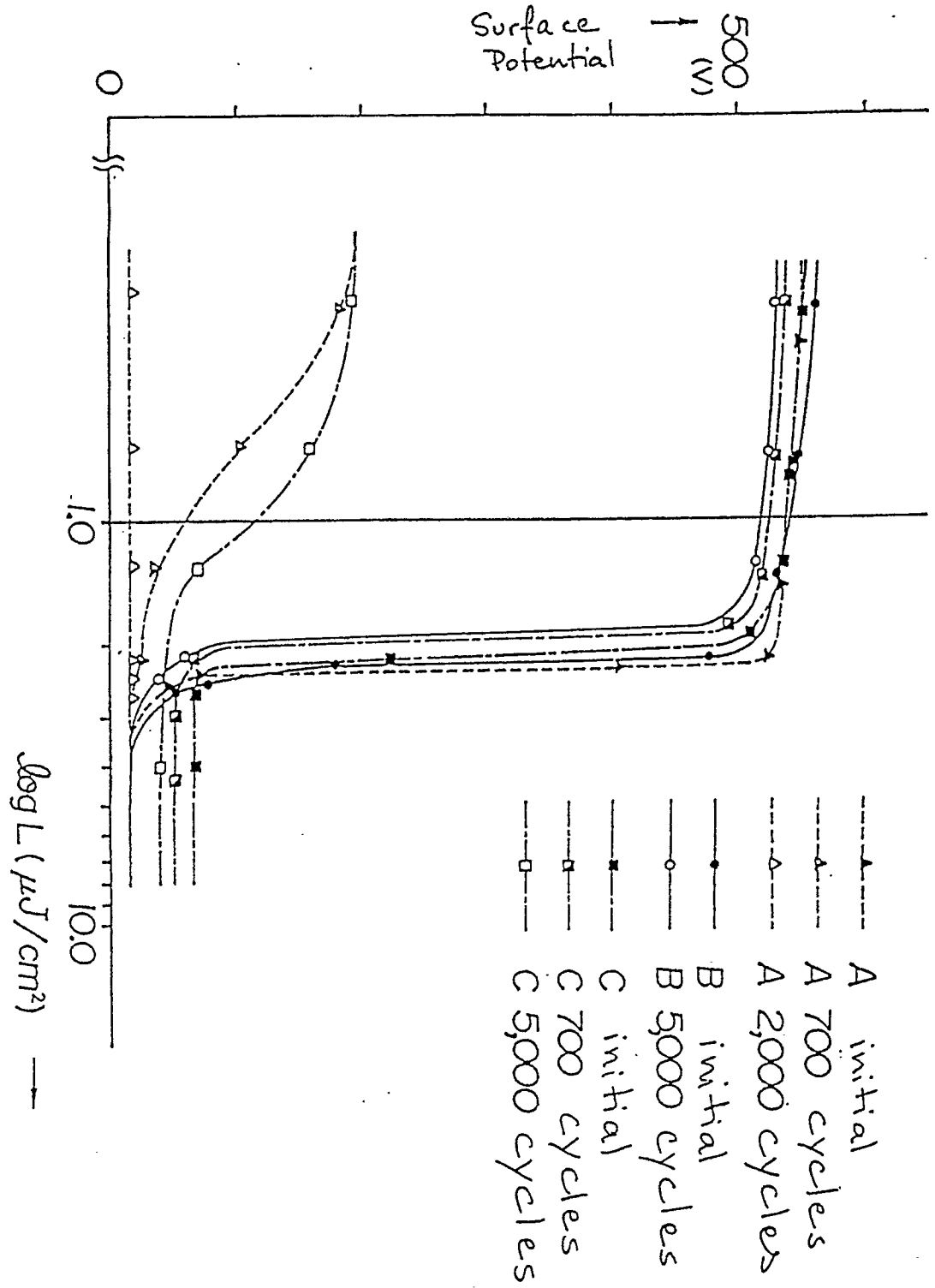


Fig. 1



