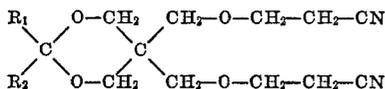




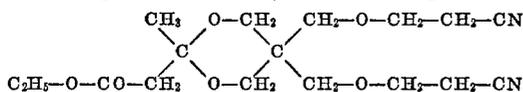
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cyclic ether grouping of the m-dioxane type. These compounds have the general formula:

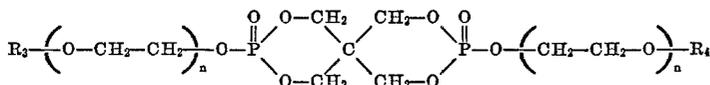


wherein  $R_1$  and  $R_2$  represent hydrogen, alkyl advantageously containing up to 6 carbon atoms, aryl, advantageously phenyl, or heterocyclic radicals, such as pyrimidine or morpholine. These groups, more especially the phenyl rings or heterocyclic radicals, can contain further substituents, such as low alkyl or alkoxy having up to 3 carbon atoms or halogen atoms such as chlorine and the like.

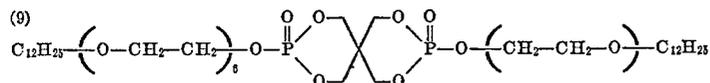
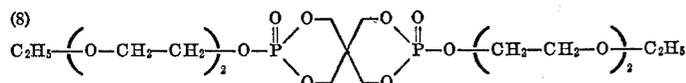
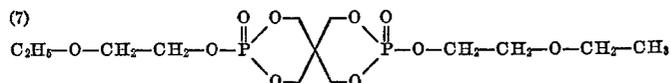
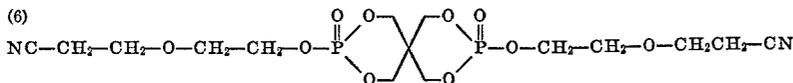
Suitable compounds and the preparation thereof are described in British patent specification No. 926,689 and the following is mentioned by way of example:



(B) Phosphoric acid esters of pentaerythritol of the formula



in which formula,  $R_3$  and  $R_4$ , which may be the same or different, represent alkyl, cyanoalkyl and especially cyanoethyl, with up to 18 carbon atoms, or aryl such as phenyl, and  $n=1-20$ , advantageously 1-10. These compounds and the preparation thereof are described in British patent specification No. 922,251, and Belgian patent specification No. 636,304. The following are mentioned as examples:



The protective layers consisting of the above three components advantageously should contain (per 100 parts of the film-forming component I such as gelatine), 5-200 parts of plasticizer and 0.5 to 10 parts of polymer. More especially suitable are those mixtures which contain 10-50 parts of plasticizers and 1-3 parts of polymer II, per 100 parts of gelatine.

In carrying out the process according to the invention, the aqueous dispersions of the polymers are incorporated by stirring, together with the plasticizers, into the binder solution which can be provided with the usual casting additives. Using this casting solution, the photographic film material is coated on the light-sensitive silver halide emulsion layer and/or on the rear side by known casting methods.

The mixing ratio between polymer proportion and plasticizer proportion depends on the required degree of roughness and can be 1:1 to 1:100, advantageously 1:5 to 1:20. The mixture of these substances is added in such a concentration to the outer protective layer that 0.1 to 5 g. per square metre are contained in the dried layer.

The protective layers should have a thickness of about 0.5 to 15  $\mu$ .

The protective layers of the invention have no deleteri-

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ous effect on the light-sensitive layers and can be used with all types of black-and-white and color photographic materials, phototechnical materials or photographic elements, which are to be used for making X-ray images.

The protective layers can be applied onto silver halide emulsion layer, filter layers, anti-halo layers, non-curling layers and the like.

There is no dependence on the composition and the number of the layers of the material coated.

#### EXAMPLE 1

To 1 litre of 1% aqueous gelatine solution ready for casting, there are added 30 cc. of 10% aqueous solution of plasticizer 1 and 1.5 cc. of a 10% aqueous polyacrylonitrile suspension (prepared by the process described in German Patent 1,058,835) and intensively mixed. This casting solution is applied to that side of a photographic film which contains the light-sensitive gelatine-silver halide emulsion layer and dried. A transparent film is obtained, which layer can be satisfactorily written on, and which has practically no tendency to become electrostatically charged.

#### EXAMPLE 2

50 cc. of a 10% aqueous solution of plasticizer 3 and 3 cc. of an aqueous suspension of a copolymer, consisting of 60 mol percent of acrylonitrile units and 40 mol percent of methyl methacrylate emulsion (prepared by the process of German Patent No. 1,058,835) are mixed and added to 1 litre of a 1% aqueous gelatine

solution which is ready for casting. This solution is cast onto the silver halide emulsion layer and the rear of a photographic material. The dried layers are free from Newton's rings when in contact with glass.

#### EXAMPLE 3

35 cc. of a 10% aqueous solution of plasticizer 7 and 15 cc. of a 10% aqueous solution of plasticizer 9 are mixed with 2 cc. of an aqueous 10% polyacrylonitrile suspension and added to 1 litre of a 1.5% gelatine solution. This mixture is cast on both sides to the silver halide emulsion layers of a photographic X-ray film. This film can be satisfactorily written on and is characterized by an excellent antistatic action, by comparison with a film material having a pure gelatine protective layer.

After air-conditioning specimens of the film at 35% relative air humidity and 20° C., the electrostatic charging in v./cm. is measured with a rotating field strength measuring instrument according to Schwenkhagen and the electric surface resistivity in ohms is measured with a knife-edge instrument.

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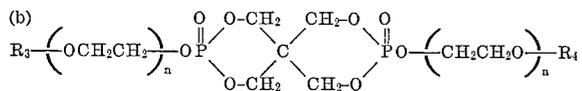
## RESULT

	Charging capacity (v./cm.)	Surface resistivity ( $10^{12}\Omega$ )
Control specimen.....	+420	13
Specimen according to Example 3.....	+5	1.5

We claim:

1. In a photographic material having a protective outer layer of a water-permeable binder containing particles of an acrylonitrile polymer having at least 50 mol percent acrylonitrile or methacrylonitrile and a grain size 1 to 25, the improvement according to which the particles are plasticized with from 1 to 100 parts of plasticizer per part of polymer, and the plasticizer is:

(a) a beta-cyanoethyl ether of a polyhydric aliphatic alcohol, or

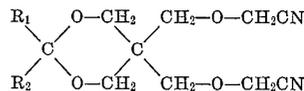


where  $R_3$  and  $R_4$  are alkyl, cyanoalkyl or phenyl and each  $n$  is a number from 1 to 20.

2. The combination of claim 1 in which the plasticizer is a beta-cyanoethyl ether of a polyhydric alcohol having up to ten carbon atoms and two to four alcohol groups.

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3. The combination of claim 1 in which the plasticizer is



in which  $R_1$  and  $R_2$  are hydrogen, alkyl containing up to six carbon atoms, or aryl.

4. The combination of claim 1 in which the plasticizer is (b) where  $R_3$  and  $R_4$  are alkyl with up to 18 carbons or cyanoethyl and each  $n$  is a number from 1 to 10.

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U.S. Cl. X.R.

96—48, 67, 87, 114