C. A. PSILANDER & T. S. SCOTT.

DYNAMO ELECTRIC MACHINE.

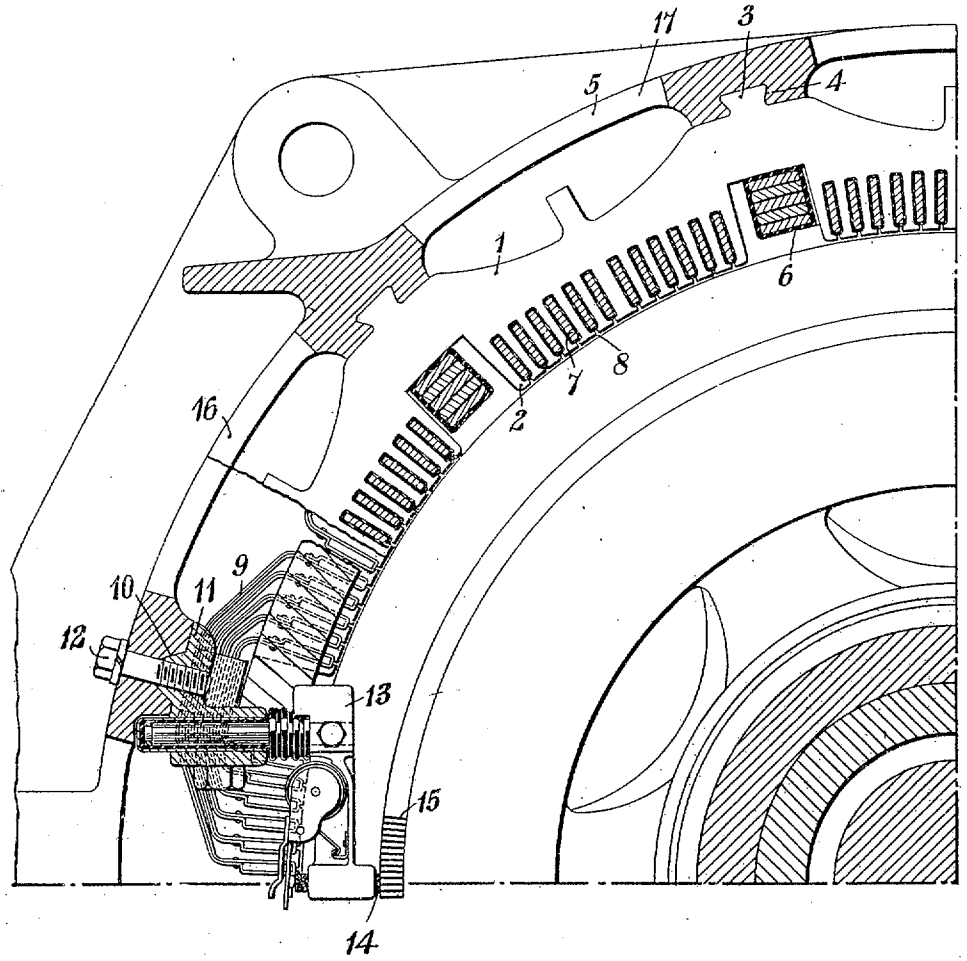
APPLICATION FILED FEB. 6, 1906.

956,543.

Patented May 3, 1910.

2 SHEETS—SHEET 1.

Fig. 1.



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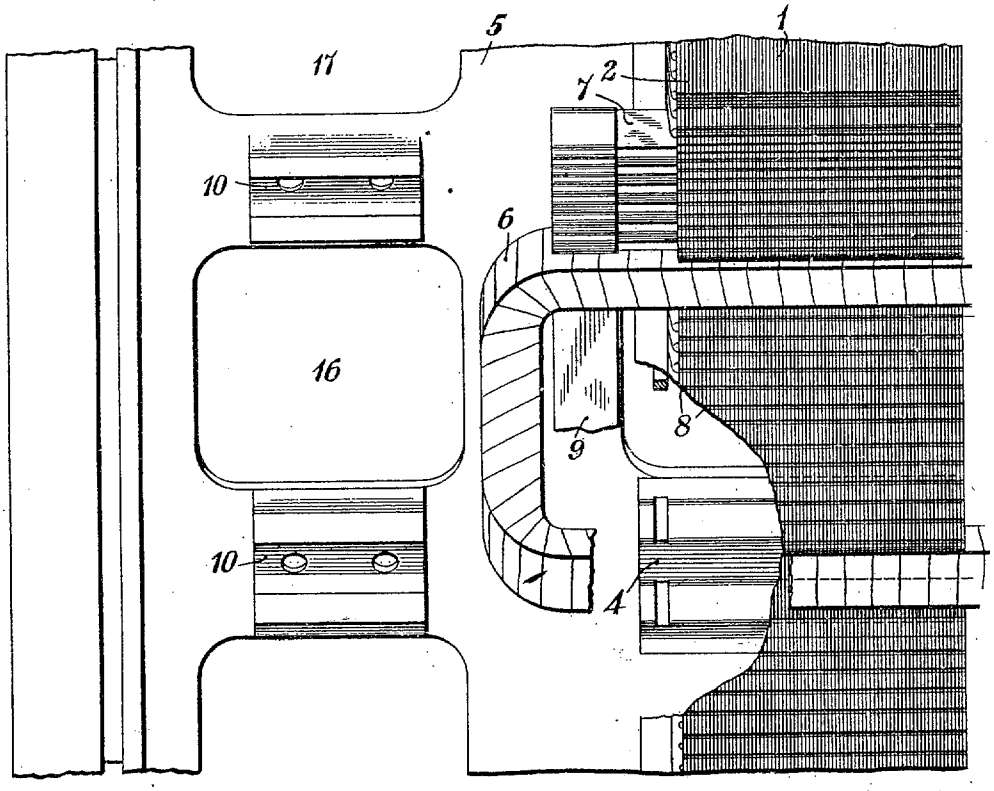
2 SHEETS—SHEET 2.

Fig. 2.



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UNITED STATES PATENT OFFICE.

WILLIAM HAY CALDWELL, OF MALLAIG, SCOTLAND.

SENSITIZED SURFACE OR FILM FOR PHOTOGRAPHIC PURPOSES.

956,567. Specification of Letters Patent. Patented May 3, 1910.

No Drawing. Application filed April 24, 1908. Serial No. 429,103.

To all whom it may concern:

Be it known that I, WILLIAM HAY CALDWELL, a subject of the King of Great Britain and Ireland, residing at Mallaig R. S. O., Inverness-Shire, Scotland, have invented Improvements in Sensitized Surfaces or Films for Photographic Purposes, of which the following is a specification.

When light acts upon certain salts of silver, for example the halogen salts, a sub-salt of silver is believed to be produced with the formation of a free substance, such as chlorin, bromin or iodin in the case of a halogen salt, but this action is at once arrested in the absence of an agent which will act as an absorbent of the substance set free.

The most active absorbents of chlorin, bromin or iodin are the so-called developing agents used in the development of photographic images, but I have discovered the curious fact that most of these agents, which are so active as to reduce the silver salts in the dark, are quite unable to render the same salts sensitive in the light by acting as halogen absorbers. The reason for this apparent paradox is that in the light and in the presence of the halogen acid formed by the halogen set free, the oxidized product of the reaction is itself again reduced with a second freeing of halogen which re-combines with the sub-salt to again form the normal salt. Thus

$$2Ag_2Br.+C_6H_4(OH)_2+2Br.=$$
$$2Ag_2Br.+C_6H_4O_2+2H\ Br.=$$
$$4AgBr.+C_6H_4(HO)_2.$$

The product chinon ($C_6H_4O_2$) in the above equation is the oxidation product of many of the substances used in development. On the other hand, substances which are not so easily oxidized as to be available for developing, are not sufficiently active as absorbers of bromin and iodin to enable them to act in such a way as to render rapid silver films made with silver bromid or silver iodid, sensitive. Thus, while the active developers which have amido (NH_2) and hydroxyl (OH) groups in the ortho (1.2), or para (1.4), positions, as for example hydroquinone and para-amido-phenol, are, for the reason given above, quite unable to absorb the free halogen resulting from the action of light on a silver haloid film, their isomerids, with the same groups in the meta (1.3) positions, as for example resorcin and meta-amido-phenol, though able to absorb the halogen without reversion taking place, cannot do this sufficiently rapidly to form a visible image in proper gradation.

At present sensitive surfaces containing silver salts belong to one or other of two classes, viz:—(1) in which the image formed by light is not visible, or only very partially so, and requires to be subsequently treated with a developer: (2) in which the image is obtained entirely by the action of light without the subsequent use of a developer.

Now the object of the present invention is to produce a sensitive surface or film having the properties of both of the above mentioned classes of surface, whereby the same surface can be caused to produce a more or less similar image either by more or less short exposure and subsequent development, or by longer exposure, the so-called printing out, without subsequent development.

At present, surfaces of the first class are made for example by heating a halogen silver salt emulsified in some vehicle, for example gelatin, the rapidity of the surfaces being determined by the degree of heating and the consequent size of the particles of silver salt aggregated into chemical contact. With such surfaces the exposure must be so regulated that no more halogen will be set free by the reduction of the silver salt than can be absorbed by the gelatin or other vehicle present, in all cases a very limited amount. Further, at present in surfaces of the second class, the halogen set free under the action of light is absorbed by an organic salt of silver, as for example an acid silver citrate in the vehicle, with formation in this case of citric acid and the normal halogen salt of silver. It is conceivable that a rapid surface might be made in this second class but hitherto this has not been found possible. A developer sufficiently active to reduce the sub-salt of a silver haloid would certainly reduce the organic silver salt in the dark, and if it be attempted to transform the organic salt, previous to development, with a soluble haloid salt, it is found that the minute quantity of sub-salt formed by the action of light is destroyed in the process, so far as its capacity for subsequent development is concerned. Further, even if it were possible to develop only the organic silver salt to form the image, the want of stability of organic compared with haloid silver salts would make the process of little value.

Now I have discovered that the organic silver salts heretofore used in the preparation of sensitive surfaces or films of the second class can be replaced by another substance by the use of which the above mentioned difficulties can be avoided and the object of the present invention attained. An ideal substance for the purpose mentioned should possess the following properties:—1. It should be incapable of reduction in the light after its oxidation by the halogen set free. 2. It should not reduce, in the dark, the silver salt employed. 3. It should absorb the halogen as rapidly as it is set free by light.

I have found that the above mentioned properties are possessed by some salts or derivatives of hydrazin (NH_2NH_2), and of hydroxylamin (NH_2OH). For example, a sensitive surface having the above mentioned properties can be prepared as follows:—In the preparation of the emulsion to form the sensitive surface, there may be used, either one of the silver haloids alone, or a mixture of two or more of them in the ordinary way. To the finished emulsion, when rapidity has been suitably adjusted by heat or otherwise, as in well known ways, there is added the necessary amount of a suitable salt or compound of hydrazin, for example a hydrazin salt of an easily oxidizable acid such as phosphorous acid (H_3PO_3), or sulfurous acid (H_2SO_3). These salts can be made by adding a solution of the acid to hydrazin hydrate ($NH_2.NH_3HO$), using methyl orange as an indicator of the completion of the reaction.

Since chlorin, bromin and iodin form a series of silver salts of gradually increasing stability, the compound of hydrazin or hydroxylamin used in the preparation of the emulsion can be determined by a consideration of such fact. For example in the case of silver chlorid, as the chlorin evolved by the action of light is a gas that is, comparatively, easily absorbed, many of the compounds of hydrazin or hydroxylamin will be found suitable for use in the manufacture of sensitive surfaces for attaining the object of this invention. For example, a sulfurous acid salt of a primary fatty hydrazin ($RNH.NH_2$), such for instance as methyl hydrazin ($CH_3NH.NH_2$) may be used. With a halogen salt of greater stability, such as silver bromid, a more active compound of hydrazin or hydroxylamin is desirable than in the case of a chlorid, such for example as the phosphorous acid salt of hydrazin hereinbefore referred to. The amount of the salt used in the preparation of the emulsion is determined by a consideration of the reducing action of the hydrazin, each molecule of hydrazin hydrate (NH_2NH_3HO), being able to reduce four molecules of silver haloid. In emulsions in which the colloid vehicle is ether-alcohol-collodion, it is necessary to use a hydrazin salt or compound which is itself soluble in ether-alcohol, and of which some of the hydrazids, for instance formyl hydrazin ($HCONH.NH_2$), are examples. From emulsions thus prepared, sensitive surfaces are then produced in the ordinary way.

Sensitive surfaces embodying the invention may also be produced by dipping sensitive surfaces prepared in the ordinary way and consisting for example of surfaces or films mounted on glass, paper or other supports or carriers, in a solution of a hydrazin or hydroxylamin salt or derivative.

Sensitive surfaces produced as hereinbefore described can be exposed in the camera for any time longer than the shortest exposure necessary, up to complete "printing out", or they can be exposed for a short time and subsequently treated with a suitable developer, such as an alkaline developer, without previous treatment with an alkaline halogen. The developer should be such that it will act slowly or quickly according as the sensitive surface has been exposed for a greater or lesser time, so that it shall penetrate all parts of the film where light has acted.

It is to be understood that the invention is not limited to the use of the particular hydrazin salts and hydrazids hereinbefore mentioned as other hydrazin salts and their fatty derivatives, as well as hydroxylamin salts and their fatty derivatives, for example hydroxylamin phosphite may be used, but excluding the aromatic compounds of hydrazin or hydroxylamin, and are to be regarded as equivalents of those mentioned. As hydrazin and hydroxylamin are two bases which may be looked upon as derived from ammonia (NH_3) by the introduction of amido and hydroxyl groups respectively, the salts and the fatty derivatives of these two bases, but excluding the aromatic compounds thereof, are hereinafter referred to generically as ammonia derivatives in some of the claims.

What I claim is:—

1. As a new article of manufacture, a sensitive photographic surface comprising a vehicle, a photographic sensitive salt and an ammonia derivative.

2. As a new article of manufacture, a sensitive photographic surface containing a silver salt and an ammonia derivative.

3. As a new article of manufacture, a sensitive photographic surface comprising a vehicle, a halogen salt, and an ammonia derivative.

4. As a new article of manufacture a sensitive photographic surface comprising a colloid vehicle, a halogen salt, and an ammonia derivative of the kind set forth.

5. As a new article of manufacture a sen-