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LIGHT SENSITIVE SYSTEMS AND PROCESSES OF MAKING THE SAME

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This invention relates to improvements in light sensitive systems and a method of producing the same. The systems, including well known silver halides, are advantageously employable for photochemical, photographical, optical and electrical purposes.

It is an object of the invention to devise a process for the production of such light sensitive systems which are obtained by fusing together the silver halides and small quantities of alien substances. This method leads to the formation of light sensitive centers in the crystallic grid or lattice of the silver halide. These alien substances introduced into the silver halide produce light sensitive centers in the crystallic grid or lattice of the silver halides, in addition to those which eventually may already be present therein and thereby induce or enhance the photosensitiveness of the product.

Light sensitive systems of this character are, for instance, described in the Stasiw specifications Serial No. 306,896 of November 20, 1939, No. 338,639, No. 338,640 and No. 338,641 of June 3, 1940.

It is also an object of the present invention to produce a light sensitive system of enhanced efficiency by incorporating a slight excess of elementary silver, beyond that required for the formation of the silver halide, in the system and to distribute this slight excess of elementary silver uniformly through the system.

The invention also has the object of enhancing the sensitiveness of such systems and of preventing decomposition, caused by a slow cooling of the same, by rapidly cooling or suddenly chilling the systems when they are in fused condition.

Other objects will become apparent from the following specification.

In principle, these light sensitive systems may be produced by fusing silver halides, as for instance, silver chloride, silver bromide, silver iodide or mixtures of the same, together with a relatively small quantity of a suitable alien substance, for example, silver sulphite or compounds which produce the same effect.

It has now been discovered that the qualities, and particularly the photosensitiveness of the systems described above and comprising silver halides combined with alien substances are considerably improved whenever the fusion of the silver halides with the alien substances is carried out in the presence of an extremely small excess of elementary silver, referred to the stoichiometric ratio of the silver in the silver halide. Through the use of this small excess of elementary silver, it had been made possible to obtain the highest degree of photosensitiveness of silver halide. Systems produced in this manner are superior, particularly as to photosensitiveness, to those light sensitive systems which are produced without the employment of this excess of silver, and for this reason, these novel systems are particularly advantageous for various technical purposes.

The present process is practically carried out for the production of highly sensitized light sensitive systems in the following way: The halogen salt of the silver is uniformly commingled with the alien substance. The mixture is heated in a suitable furnace to such temperature as will lead to fusion and eventually to a combining reaction of the ingredients, and during this heating operation, an excess of silver, beyond that required by the halogen is produced, in some suitable way. After the fusion has taken place, the temperature is reduced again. In this manner, there is obtained a photosensitive product composed of silver halide and an alien substance.

The operations of heating and cooling the silver halide and alien substances may be repeated once or a plurality of times.

The production of an excess of silver may be accomplished in various ways.

The quantity of silver required may, for instance, be introduced in the form of a silver compound. For example, nitrate of silver, carbonate of silver, oxide of silver or other compounds containing silver may be introduced into the fused mass of silver halide and alien substances at the desired temperature.

The silver compound, however, required to furnish the excess silver may even be added to the starting materials themselves prior to their intermixture. This silver compound may, therefore, be added to the silver halides or to the alien substances or to both of them.

Furthermore, the process may be carried out by utilizing as starting materials some silver halides and/or some alien substances which contain silver in excess, as compared with the stoichiometric ratio of anion and silver. This additional silver content may either be chemically bound to either of the ingredients of the mixture or it may adsorptively be retained thereon. The commercially available silver halides frequently contain additional silver compounds, due to the manner in which the silver halides had been produced. In determining the excess of silver which the finished light sensitized product is to have, this content of additional silver compounds in

the silver halide must be taken into consideration.

Another way leading to a content of excess silver in the end product of the process consists in regulating the fusing operation for uniting the silver halide and alien substances in a predetermined way. This modification or regulation of the fusing process involves the selection of such temperature conditions and such duration of the heating, that a slight decomposition or conversion of one or more of the ingredients is effected, namely to that extent only which is required for furnishing the slight excess of elementary silver. For instance, upon employing silver sulphide as an alien substance, products of complex physical or chemical characteristics are formed which comprise elementary silver and silver sulphides.

Another way of producing an excess of silver in the highly sensitized product consists of adding the necessary quantity of an substance which may reduce silver compounds to metallic silver to the halides of silver while they are in fused condition. For instance, copper and other suitable metals or their compounds may be selected.

Another possibility of producing an excess of silver consists of decomposing the silver halides by exposing them to light. It is well known that this exposure leads to the decomposition of the silver halide to silver and liberated halogen. The length and intensity of the exposure required for production of the desired excess of silver will have to be determined by tests in each case.

The quantity of the excess of silver to be employed, according to the present invention, is a very small quantity. This quantity may approach the quantitative value of the alien substances required for producing the photosensitiveness of the silver halide. If there should have been formed an excess of silver greater than desired, this over-excess must again be eliminated. The quantity of the excess of silver will depend upon the kind of the light sensitive systems to be improved and upon the character of those substances which are used to create this excess of silver therein.

For producing the photosensitive systems of the present invention, silver chloride, silver bromide and silver iodide may be used alone or mixtures of the same may be employed. When using mixtures, the quantities of the different silver halides must be selected in accordance with the conditions present in each case.

The alien substances employed for the creation of the light sensitive "centers" may, for instance, be silver oxide, silver nitrate, silver sulphide, silver selenide, silver cyanide, silver cyanate, and other silver compounds. Furthermore, it has been found that compounds of other metals, as for instance, compounds of copper, such as copper chloride, copper bromide and other compounds induce the formation of photosensitive centers in silver halide.

The quantity of alien substances to be added for this purpose to silver halide is very small, as well known in the art. The quantity is different with different light sensitive systems, and in each case must be selected in accordance with the peculiarities of the system. Similarly also the type or character of the alien substance must be selected in dependency upon the peculiarity of the light sensitive system to be produced. These alien substances may be introduced as individual compounds or as mixtures of such compounds into the silver halides.

Instead of the alien substances being added in the form of complete compounds, they may be produced within the fused mass itself. So for instance, silver sulphide may be produced and simultaneously incorporated with the silver halides by passing vapors of sulphur or any other gases generating silver sulphide over the fused mass of silver halides. Other alien substances also may be produced correspondingly and directly by cooperation with the fused silver halides.

Very frequently it had been observed that light sensitive systems produced at high temperature are more or less dissociated to the form of their original ingredients when they are cooled. This condition results in a reduction or loss of their photosensitiveness.

The present invention constitutes a process of producing systems of this type without running the risk of reducing the photosensitiveness. For this purpose, the present process refrains from slowly cooling the heat prepared products of silver halides and alien substances, but instead it suddenly chills these products. Owing to this sudden chilling, the conversion of the systems to those components of which they were built up is impeded, and there remains as a stable product solely the highly sensitive silver halide systems. The chilling operation of the heated products, which in most instances are in fused condition may be effected in the ordinary way, as for instance, by pouring them into cold liquids, by spraying them into air or into other gases through suitable nozzles, or through other chilling methods. It is also feasible to first comminute the heated masses, and then to treat them in finely divided condition with solid liquid of gaseous chilling media.

Upon repeatedly heating silver halide commingled with alien substances, it is obvious that the chilling operation may be resorted to after each heating.

The light sensitive systems of the present invention in their completed condition form either fused masses or sintered masses or powders which can be reduced to the desired granular size. Where comminution is required, this comminution may be carried out in the usual way by grinding and similar processes. One method of comminution which has proved advantageous is, for instance, the operation of atomizing the light sensitive systems while they are in fused condition.

The comminution by spraying or atomizing of the fused masses may be effected either by direct atomization of the compounds in fused condition under pressure, or by subjecting the fused mass discharged in jet form from some opening to the action of atomizing media, as for instance, to a jet of gas or vapor directed upon the jet of the fused mass. Obviously other methods of atomization may be employed.

The atomization of the fused light sensitive systems may, therefore, be produced by known means. Single as well as multiple atomizing apparatus may be employed. It is advisable to employ a plurality of atomizers in parallel arrangement so as to have continuous operation. It is, furthermore, feasible to combine some producing steps themselves, for instance, the chilling step with the atomizing step.

Atomization may also be effected in a closed or cyclic process, inasmuch as the gases after effecting atomization may be recovered and returned to the atomizing apparatus by a suitable pressure or suction device, while a loss of gases may be suitably compensated for. When combining

atomization with the production itself of the photosensitive silver halides, it may become advisable to provide a device for absorbing that halogen which becomes free.

The present process can be varied in many ways. One modification of the process, when employing silver chloride, silver bromide or both, or mixtures containing the same rests in the fact that silver iodide is added to the photosensitive systems embodying silver chloride and/or silver bromide. The mixture of the silver halides produced in this manner is then treated at temperatures not above 150° C. The addition of the silver iodide may be affected in any desired way. It may be added, for instance, to the initial ingredients either before or during the introduction of the alien substances. It may also be introduced, however, into the light sensitive systems after they have been converted to liquid or solid consistency. It is essential that the introduction of the silver iodide into the other silver halides is carried out in such manner as to produce a uniform thorough intermixture of the ingredients.

In the production of these photosensitive systems, there occur occasionally nuclei or centers which contain silver and which, upon development, lead to fogging. These silver nuclei may be eliminated for instance by an oxidizing treatment of the light sensitive systems.

This oxidizing treatment may be carried out in various ways and with various oxidizing means, as described in application Serial No. 338,641, of June 3, 1940. Solid substances, liquid, gases or vapors may serve as oxidizing media. It may be carried out with oxygen itself, and the treatment can be effected at elevated temperatures and pressures. The oxidizing media must be such as to be inert with respect to those alien substances to which the photosensitiveness of the silver halide is due.

The oxidizing treatment may be combined with the production itself of the photosensitive systems. For this purpose, the production of the systems may take place entirely or partly within an oxidizing atmosphere. Then again, it is feasible to subject the finished products to oxidizing treatment. By way of example, it may be stated that oxidizing gases or vapors are conveyed through the fused mass or over the same, and this passage of the gases or vapors may be effected at elevated pressures. When light sensitive systems of solid conistency are to be treated for oxidation, it is also necessary to operate at higher temperatures and pressures. The production of light sensitive systems in the presence of oxidizing media and the oxidizing treatment of the systems after their production may be combined with each other where this seems desirable.

The length of the oxidizing treatment, the temperatures and pressures to be employed are dependent upon the type of the ingredients used and upon the type of the light sensitive systems to be produced and must be selected accordingly. Under all conditions, they must be selected from the viewpoint of leaving the alien substances unaltered.

The action of the oxidizing media, for instance, oxygen, may be catalized by adding to them small quantities of other substances. Thus, for instance, the addition of potassium iodide, potassium bromide, alkali iodates and the like will enhance the speed of the reaction of the oxygen and other oxidizing media.

Finally, the oxidation treatment may be combined with the atomization of the light sensitive systems, referred to above, inasmuch as the atomization may be carried out by means of oxidizing gases or vapors or both of them.

The elimination of those nuclei which contain silver and which induce fogging may also be induced in other ways, for instance, by binding the silver to halogen, halogen compounds and other materials or proper action.

Example

Silver bromide, approximately 10 gram, is heated in an electric furnace to a temperature above the fusion temperature of the silver bromide, in the presence of small quantities of silver sulphide, for instance, one milligram, and of approximately the same quantity of potassium iodide or potassium bromide and in the presence of about 0.5 gram silver iodide. The fused mass is atomized by means of oxygen in a suitable sprayer. The powder resulting from this step is not given time to cool, but is immediately and suddenly chilled to room temperature in a chilling receptacle positioned closely, and it is then collected on a filter of sintered glass. This powder then is heated in a furnace for about two hours, at a temperature of about 100° C and in an atmosphere of oxygen, while the pressure is a normal or higher one. After cooling, the product constitutes a system of high light sensitiveness.

The process of the present invention, however is not limited to the production only of light sensitive systems. This process also permits to regenerate light sensitive systems originally produced by the present process and which had entirely or partly lost their light sensitiveness by exposure to light. For the purpose of regeneration, the light sensitive systems which had lost their sensitiveness entirely or partly are subjected to the same steps of heating and chilling and also to the other features of the original process of production or its variations, as outlined above. The light sensitive products are then again restored to the high degree of sensitiveness.

The light sensitive products of this process are employed without any special binders, for instance, by being applied to suitable carriers by means of an adhesive. They also can be incorporated with carrier colloids in finely divided condition. This step leads to the formation of emulsions similar to photographic emulsions. The mixtures of the light sensitive systems with the colloids can be poured out in layers or can be applied in some other form to any suitable carriers or bases, foils and the like.

When the light sensitized products are to be dispersed in a binder, this dispersion is carried out by thorough intermixture, as for instance, agitation, by vibratory treatment and/or by making use of dispersing agents of the type known in colloidal chemistry, by wetting agents, dispersing agents and the like.

When these emulsions consisting of silver halides and binders are to be poured, this pouring operation can be effected in the manner known from the production of photosensitized photographic films, plates, papers and the like. The emulsions can be poured in one or a plurality of layers. The usual production precautions must be provided as back pourings, adhesive and subbing layers, covering or protective layers, anti-halation layers, intermediate layers, filtering layers and the like. Again, optical sensitiz-

ing agents and dyes may be employed for sensitizing and coloring the emulsions and layers.

Suitable carrier colloids are the various types of gelatine, also the so-called inert gelatine, albumins and other proteic materials, collodion, cellulose esters, cellulose ethers, cellulose, synthetic resins, polymerization products and the like.

The bases or supports for the emulsions made up for the light sensitive systems and colloids may be formed by glass, films of cellulose, cellulose esters and ethers, by resins, polymerization products, metal foils, papers and the like.

The emulsions are poured upon their bases by processes which are generally known in the photographic industry for the production of emulsionated plates, films, papers, etc.

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