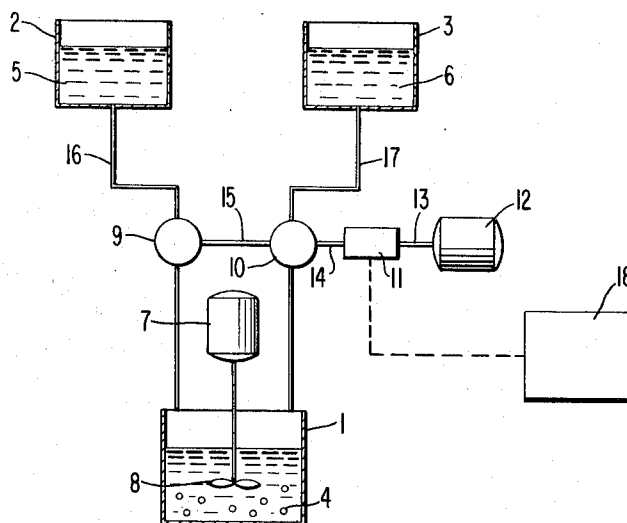


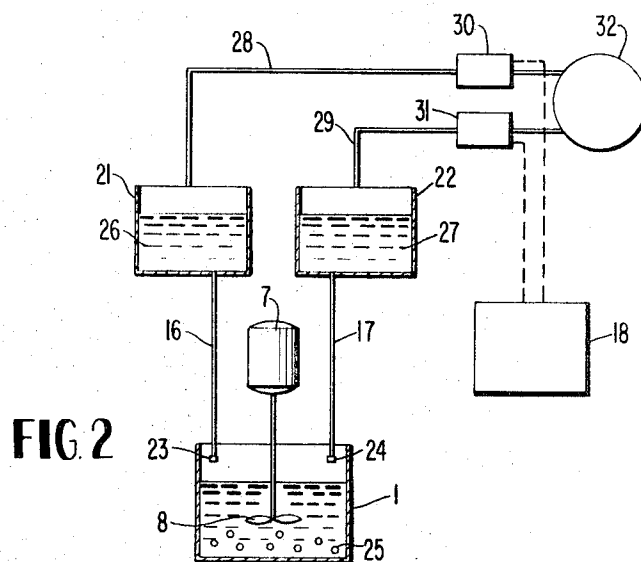
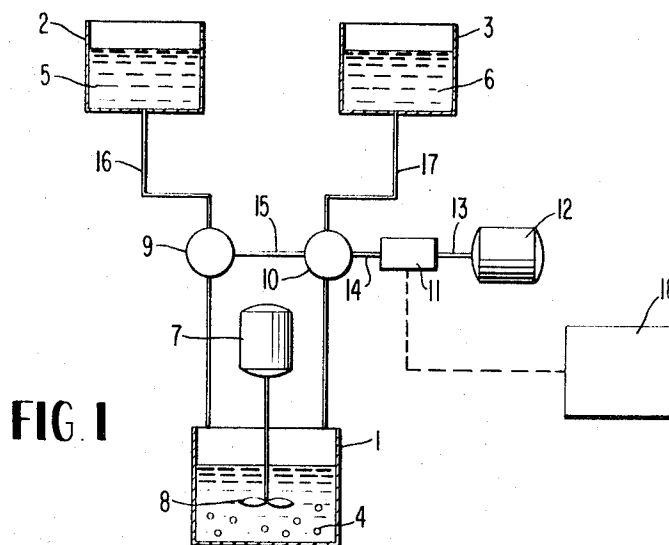
[54] **PREPARATION OF INORGANIC SALT CRYSTALS**[72] Inventors: **Kazuo Irie; Keiichi Suzuki**, both of Kanagawa, Japan[73] Assignee: **Fuji Photo Film Co., Ltd.**, Ashigara-Kamigun, Kanagawa, Japan[22] Filed: **Oct. 23, 1968**[21] Appl. No.: **769,983**3,031,304 4/1962 Oliver.....96/94
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Jan. 30, 1968 Japan.....43/5556[52] **U.S. Cl.**.....96/94 R, 23/61, 23/87 R,
96/114.7, 96/115 R[51] **Int. Cl.**.....G03c 1/02[58] **Field of Search**.....96/94, 115 R, 114.7; 23/61,
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[57] **ABSTRACT**

An improved method for preparing crystals of a weak-soluble inorganic salt, using a double decomposition of two or more inorganic salts by simultaneously adding aqueous solutions of the inorganic salts to a dispersing medium under conditions of agitation, which comprises increasing the rate of addition of the aqueous solutions of the inorganic salts which are reacted at a rate which is proportional to, or less than, the growth rate of the surface areas of the growing crystals. Particular applicability is found wherein the salt is a silver halide and the dispersing medium is an aqueous gelatin solution.

11 Claims, 2 Drawing Figures



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PREPARATION OF INORGANIC SALT CRYSTALS

BACKGROUND OF THE INVENTION

1. Field of the Invention:

The present invention relates to a process for the production of the crystals of an inorganic salt, and more particularly to a process for growing the crystals of a weak-soluble inorganic salt.

2. Description of the Prior Art:

There has hitherto been employed a method of preparing the crystals of a weak-soluble inorganic salt, such as cadmium carbonate or a silver halide, by the double decomposition of two or more inorganic salts in the presence of a protective colloid such as gelatin. To prepare the crystals of a weak-soluble inorganic salt having a uniform grain size and a uniform shape by such a conventional method, two or more types of aqueous solutions of inorganic salts which are to be reacted must be gradually and simultaneously added to a dispersing medium, such as an aqueous gelatin solution, at a constant rate. Therefore, it takes a very long period of time to complete the reaction, which makes the method inefficient.

SUMMARY OF THE INVENTION

It has been found that crystals of a weak-soluble inorganic salt which have a uniform grain size can be obtained in a shortened period of time in a process which comprises utilizing a double decomposition of two or more inorganic salts by simultaneously adding aqueous solutions of the salts to a dispersing medium under conditions of agitation by utilizing the improved steps which comprise increasing the rate of addition of the aqueous solutions of the inorganic salts which are reacted at a rate which is proportional to, or less than, the rate of growth of the surface areas of the growing crystals of the weak-soluble inorganic salt which is formed.

Thus, an object of the present invention is to provide an improved method of preparing the crystals of a weak-soluble inorganic salt, having a uniform grain size, in a reduced period of time.

Another object of this invention is to provide a photographic gelatino silver halide emulsion containing the crystals of a silver halide having a uniform grain size, also at a reduced period of time.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic view showing an embodiment of the apparatus which may be utilized to practice the present invention;

FIG. 2 shows a second embodiment of the apparatus which may be utilized to practice the process of this invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

According to the method of this invention, when preparing the crystals of a weak-soluble inorganic salt by simultaneously adding two or more aqueous solutions of inorganic salts which are to be reacted to a dispersing medium, the rate of addition of the aqueous solutions is increased at a rate proportional to, or less than, the rate of growth of the total areas of the growing crystals of the weak-soluble inorganic salt.

As mentioned above, in the general method conventionally employed, the double decomposition of two or more inorganic salts is reacted to form the crystals of a weak-soluble inorganic salt by gradually and simultaneously adding two or more aqueous solutions of the inorganic salts which are to be reacted at a substantially constant rate to a dispersing medium.

In contradistinction, with the method of this invention, the rate of addition of the aqueous inorganic salt solutions is varied throughout the double decomposition reaction of the inorganic salts, that is, when the total surface areas of the crystals of the weak-soluble inorganic salt (which are growing due to the addition of the aqueous inorganic salt solutions) are increased, the rate of addition of the aqueous solutions of the inorganic salts is increased, in proportion to the rate of growth of the total surface areas of the crystals.

In the above case, the increase in the rate of addition of the aqueous inorganic salt solutions with the increase in the total surface areas of the crystals of the weak-soluble inorganic salt may be conducted continuously, but it may also be conducted stepwise, as the case may be.

The method of this invention may also be carried out in the presence of a solvent for the weak-soluble inorganic salt, such as aqueous solution of ammonia.

The process of this invention may also be applied to the production of various weak-soluble inorganic salts, such as cadmium carbonate, but it is more profitably applied to the preparation of a photographic gelatino silver halide emulsion containing the crystals of a silver halide, such as, silver bromide, silver chloride, silver iodobromide, silver iodochloride, and the like, which has a uniform and relatively large grain size, as well as other photographic emulsions containing inorganic salt crystals, such as cadmium carbonate.

The method of this invention will now be explained with reference to the accompanying drawings, in which:

FIG. 1 is a schematic view showing an embodiment of this invention; and

FIG. 2 is a schematic view showing a second embodiment of this invention.

In FIG. 1, an aqueous gelatin solution is stirred in a vessel 1 by means of a stirrer 8 driven by a motor 7. An aqueous silver nitrate solution 5 and an aqueous alkali halide solution 6 stored in a tank 2 and tank 3, respectively, are added to the aqueous gelatin solution through a conduit 16 and a conduit 17 by means of supplying pumps 9 and 10, respectively. In one embodiment of this invention (shown in FIG. 1), the supplying pumps 9 and 10 are driven by means of a motor through a transmission shaft 13, a speed change gear 11, and transmission shafts 14 and 15, the speed change gear 11 being connected to a programmer 18. In the formation of a weak-soluble inorganic salt, such as a silver halide, by reacting two or more types of inorganic salts in a dispersion medium, the surface areas of the crystals of the weak-soluble inorganic salt thus formed are generally increased as time passes. Hence, by preliminary experimentation, the relationship between the surface area and time should be determined, and the results should be recorded, whereby the surface areas of the growing crystals of the weak-soluble inorganic salt can be determined by the amount of time which has passed since the start of the reaction.

Thus, by continuously increasing the rate of rotation of the supplying pumps 9 and 10 through the speed change gear 11 in response to a speed change signal from the programmer 18 (set according to the predetermined relationship between the surface areas and time) the amounts of the aqueous silver nitrate solution and the aqueous alkali halide solution which are added can be gradually increased in proportion to the growing surface areas of the crystals, whereby crystals 4 of a silver halide having a uniform grain size are formed.

In the other embodiment of this invention (shown in FIG. 2), an aqueous sodium carbonate solution 26 and an aqueous cadmium chloride solution 27, stored in a tank 21 and tank 22, respectively, are supplied through conduits 16 and 17 to an aqueous gelatin solution stirred by means of a stirrer 8 and pump 7 in a vessel 1. Throttle plates 23 and 24 are mounted on the ends of conduits 16 and 17, respectively, to aid in flow control. The supplements of aqueous solutions 26 and 27 are conducted by sending compressed air from an air compressor 32 through conduits 28 and 29 via pressure-controlling means 30 and 31, which are connected to a programmer 18. By stepwise increasing the air pressure in the spaces 21 and 22 in the tanks 26 and 27, in accordance with the pressure changing signal to the pressure control means 30 and 31 from air compressor 32, the amount of the aqueous solutions of the inorganic salts are stepwise increased, whereby crystals 25 of cadmium carbonate having a uniform grain size are formed.

In the above examples, the invention is explained with reference to only a few embodiments, but it will be understood that many other variations may be employed within the scope of this invention. For example, in the embodiment shown in

FIG. 1, the amounts of the two aqueous inorganic salt solutions are controlled simultaneously by one driving system, but the control of the amounts of the inorganic salts may also be performed by varying the amount of only one of the aqueous solutions of the inorganic salts, or it may be controlled by varying both solutions separately. Moreover, the means for controlling the amounts of the aqueous inorganic salts is not limited to a speed variable supplying pump or an air pressure control means, but other means may be employed, for example, the amounts of the solutions supplied may be controlled by controlling the levels of the aqueous solutions in the tanks by raising the tanks.

As mentioned above, the method of this invention enables the production of the crystals of a weak-soluble inorganic salt having a uniform and relatively large grain size and these can be obtained in a very short period of time.

The following non-limiting examples are given in order to illustrate the invention.

EXAMPLE 1

To 1,000 ml. of an aqueous 3 percent gelatin solution there was added, while adequately stirring certain amounts of an aqueous 1 N silver nitrate solution and a 1 N potassium bromide solution. The following addition method was used. The rate of addition of the aqueous solutions was increased proportionately to correspond to the increase in the total surface area of the silver bromide crystals formed. Uniform silver bromide crystals having a grain size of 0.4 micron were obtained.

Passage of time	Total solution amount from the start
10 min.	10 ml.
20	35
30	90
40	190
55 (finished)	410

The reaction was completed in 55 minutes. It will be understood from this example that production time can be markedly shortened according to the process of the invention, when compared with the known method wherein the rate of addition of the aqueous silver nitrate and the potassium bromide solutions are not changed during the reaction. Using reaction solutions having the same compositions as those of this example, it took about 7 hours to obtain a silver bromide crystal of 0.4 microns in size.

EXAMPLE 2

To 1,000 ml. of an aqueous 7.5 percent gelatin solution were added, while stirring adequately, an aqueous 0.6 N sodium carbonate solution and a 0.6 N cadmium chloride solution. The following conditions were used to thus obtain cadmium carbonate crystals having a grain size of 6 microns.

Addition Speed	Addition Time
0.6 ml./min.	16 min.
2	20
5	20
10	10
25	10
Total:	76

By the process of this invention, a cadmium carbonate crystal of a 6-micron size, having a quality similar to the crystal produced by a known method, was produced in a time of about 1/10 (or less) of that produced by the known method, which took about 13 hours.

To further define the invention, it should be noted that the term "weak-soluble" salt can be defined by the equation $pK = \log 1/K$, and this should be equal to or greater than 4. K , of

course, is the dissociation constant of the material, this figure being readily available in any standard text.

In the examples, substantially equivalent amounts of each of the materials were added after the seeds of the crystals formed. Of course, as indicated, the increase in the addition rate is proportional thereafter to the surface area of the crystals. This may be easily determined by a slight amount of empirical experimentation, well within the ambit of one skilled in the art. The size of the individual crystal grains is easily determined.

What is claimed is:

1. In a method of growing crystals of a weak-soluble inorganic salt wherein the solubility thereof is defined by the equation $pK = \log 1/K \geq 4$, wherein K is the dissociation constant, by the double decomposition of two or more inorganic salts by simultaneously adding aqueous solutions of the inorganic salts to a dispersing medium under conditions of agitation, the improvement which comprises:

increasing the rate of addition of the aqueous solutions of the inorganic salts which reacted to provide the crystals of the weak-soluble inorganic salts from an initial value at the beginning of crystal growth at a rate which is proportional to the growth rate of the surface areas of the growing crystals of the weak-soluble inorganic salt, whereby crystals having a uniform grain size are rapidly obtained.

2. The method as claimed in claim 1 wherein said weak-soluble inorganic salt is a silver halide and said dispersing medium is an aqueous gelatin solution.

3. The method as claimed in claim 1 wherein said weak-soluble inorganic salt is cadmium carbonate and said dispersing medium is an aqueous gelatin solution.

4. The method of claim 1 wherein the increase in the addition rate of the aqueous solutions of the inorganic salts which are reacted is conducted continuously in proportion to the time passed since the start of the double decomposition reaction.

5. The process of claim 1 wherein said dispersing medium is a binder such as is used to form silver halide emulsion layers in the photographic art.

6. The method of claim 1 wherein said inorganic salts which are double decomposed include a silver salt and a salt which will react therewith to yield a silver halide, said dispersing medium is an aqueous gelatin solution as is used in the photographic art, and said weak-water-soluble inorganic salt is a silver halide.

7. The method of claim 6 wherein said silver salt is silver nitrate and said salt which will react therewith is an alkali halide.

8. The method of claim 3 wherein the inorganic salts which are double decomposed comprise sodium carbonate and cadmium chloride.

9. The method of claim 1 wherein said increasing is step-wise.

10. In a method of growing crystals of a weak-soluble inorganic salt wherein the solubility thereof is defined by the equation $pK = \log 1/K \geq 4$, wherein K is the dissociation constant, by the double decomposition of two or more inorganic salts by simultaneously adding aqueous solutions of the inorganic salts to a dispersing medium under conditions of agitation, the improvement which comprises:

increasing the rate of addition of the aqueous solutions of the inorganic salts which are reacted to provide the crystals of the weak-soluble inorganic salts from an initial value at the beginning of crystal growth at a rate which is less than the growth rate of the surface areas of the growing crystals of the weak-soluble inorganic salt, whereby crystals having a uniform grain size are rapidly obtained.

11. The method of claim 10 wherein the increase in the addition rate of the aqueous solutions of the inorganic salts which are reacted is conducted continuously in proportion to the time passed since the start of the double decomposition reaction.

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