

On Mechanism of Silver Halide T-crystals Nucleation and Growth

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Abstract

The process of T-crystals formation includes at least three stages, and the absence though by one of them makes occurrence of T-crystals impossible. These stages are nucleation, transformation of nucleus into a T-crystal and growth of T-crystals.

Introduction

The silver halide T-crystals are widely used in modern photographic materials. However till now there is no conventional opinion on such crystal's process of formation and growth. Only rather recently was shown the importance of coalescence processes at the first stage of T-crystals formation^{1,2}. There is open the question on driving forces of a mass transfer at the stage of T-crystals growth. For example, idea about the dependence of the T-crystals shape from amount of twin planes has not confirmed³. Recently the concept, explaining occurrence of T-crystals different shapes by presence of different amount of surfaces (100) and (111) on their lateral sides was offered⁴. However while this idea has fail of general support. In particular it is not clearly why at presence of sides (111) the speed of T-crystals lateral growth at $pBr=3,0$ was reduced up to a minimum. That's why the research of the silver halide T-crystals formation mechanism attracts steadfast attention of the explorers.

Experimental

We use a method of a fine emulsions physical ripening as a method of photoemulsion silver halides T-crystals reception. In our experiments we try to determine interrelation of the received T-crystals dispersion characteristics with conditions of initial fine emulsion synthesis and with conditions of a physical ripening realization.

At the first stage by a control double jet crystallization the fine silver halide emulsion (size of microcrystals - less than 100 nanometers) is received. Then this emulsion subjected to a physical ripening under control conditions. A physical ripening is conducted up to complete disappearance of initial fine emulsion microcrystals. The dispersion characteristics of received T-crystals are

estimated on microphotos of photoemulsion samples carbon replicas, received on an electronic microscope.

Experimental Results and Discussion

On the basis of received experimental date we have come to the conclusion that process of silver halide T-crystals formation includes, at least, three stages:

- Formation of a T-crystal "nucleus";
- Transformation of "nucleus" into a T-crystal;
- Growth of the T-crystal.

Each of this stages has the peculiarities, but at the same time, the absence though by one of stages makes process of T-crystals formation impossible. We shall consider these stages in more details.

Formation of a T-crystal "nucleus"

It is impossible to explain the process of T-crystals occurrence and growth during a fine emulsions physical ripening without attraction of the "nucleus" concept. Really, how among all close on the size microcrystals some of these crystals begin heavily and anisotropically to grow? It is obvious, that the part of fine emulsion microcrystals should differ on the properties from common crystals. The share of these "nuclei" and, hence, dispersion characteristics of T-crystals, are determined by conditions of fine emulsions synthesis, instead of physical ripening realization conditions.

Investigations of the last years have shown, that the formation of particles, distinguished on properties from common fine emulsions microcrystals, proceeds mainly at the coalescence of generated grains¹. Was shown, that than the condition of fine emulsion crystallization is closer to ideal and the above concentration of gelatin, the will be less in this fine emulsion formation of growth centers - T-crystals "nuclei"².

In the other hand, it is considered that the final T-crystals have a plane inner imperfections which is attributed to a twin plane. In our opinion, such assumption is questionable. It is proved that formation of so called "twinned" crystals takes part during precipitation due direct coalescence of the grains (Figure 1a). It results in formation of coalescent plain of untwinned nature. Since this plane is parallel to the crystallographic planes (111) of the T-crystals we can to assume that it appear due to junction of the (111) faces, namely of octahedral grains.

The moving forces of such coalescence may be the differences of microcrystals surface charge. It was shown, that the coalescence processes take part for the silver bromide fine emulsions during physical ripening in the isoelectrical point of silver bromide, whereas this emulsion remains stable during physical ripening at the another pBr value⁵. The change of surface charge may occur in the region of silver nitrate solution injection, connected with the region of silver ion excess.

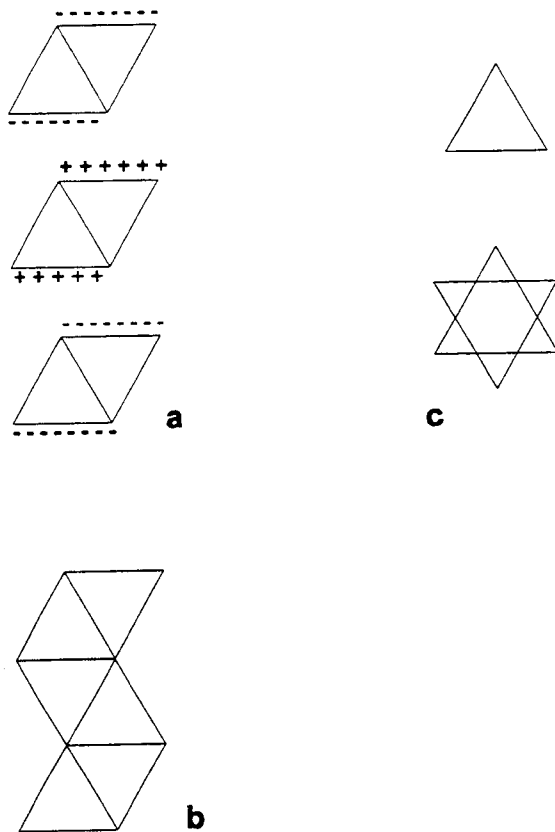


Figure 1. T-crystal "nucleus" formation on coalescent mechanism: a - interaction of fine crystals with different surface charges; b - resulting nucleus with reentrant structures; c - possible location of contacting (111) faces.

As to T-crystal nucleus, it has reentrant structure and the coalescence plane can possess an axis of third or sixth order (Figure 1b, 1c). Therefore we have differences in T-crystals side faces structure from the beginning of their formation. In dependence on this order a hexagonal or triangular shaper primary T-crystals forms through the diffusion controlled growth.

Transformation of "nucleus" into a T-crystal

As is known, the T-crystals formation and growth occur only in certain conditions⁶. Therefore the "nuclei" occurrence is first, but not unique stage necessary for T-crystals formation. Was shown, that the kinetic dependence of T-crystals average size change during fine emulsion physical ripening is expressed S-shape⁷.

The presence of induction period is caused by presence of a stage of the primary T-crystal "nucleus" transformation into a T-crystal, and the most probable mechanism of a mass transfer is ion diffusion through a solution. If additional amount of fine emulsion have been put to T-crystal emulsion, the present T-crystals will laterally growth and additional T-crystals will not form. This effect is conditioned by the greater rate of lateral T-crystal growth than diffusion-controlled growth of initial "nuclei". The T-crystals formation even at presence of T-crystals "nuclei" in fine emulsion does not occur in conditions, when the ionic growth is retarded.

As an example it is possible to demonstrate comparative results of a silver bromide fine emulsion physical ripening at the presence of bromide ions excess ($pBr < 1.5$) and at the presence of potassium thiocyanate (see Table 1). A ripening of silver bromide fine emulsion results in formation of T-crystals in both cases⁸. However the silver bromide T-crystals will be formed only at only at low pBr value. At the presence of potassium thiocyanate and at $pBr > 2.0$ silver bromide fine emulsion physical ripening does not result in T-crystals formation, though the silver bromide lateral shell formation proceeds without complication. Other words, it is blocked not the growth process of silver bromide T-crystals, but the stage of "nuclei" transformation into T-crystals.

Table 1. Influence of fine emulsion crystals composition and physical ripening conditions on T-crystals formation.

No.	Source emulsions	Physical ripening conditions	Resulting emulsions
1	AgBr fine	$pBr=1.0$; [KSCN]=0.04 M	AgBr T-crystals
2	AgBr fine	$pBr=2.5$; [KSCN]=0.04 M	AgBr T-crystals
3	AgBr(I) fine	$pBr=1.0$; [KSCN]=0.04 M	AgBr(I) T-crystals
4	AgBr(I) fine	$pBr=2.5$; [KSCN]=0.04 M	No T-crystals
5	AgBr T-crystals + AgBr(I) fine	$pBr=2.5$; [KSCN]=0.04 M	AgBr T-crystals with AgBr(I) shells

Another example gives the investigation of iodide ion's distribution in T-crystals, created by the fine emulsions physical ripening method⁹. Technique of a "differential dissolution" allows to reveal unhomogeneity of iodide ion's distribution in model silver bromoiodide T-crystals. The areas with low concentration of iodide ions are placed in T-crystals chaotically, however common law is the presence of a similar site in center of T-crystal, irrespective of this crystal shape and size.

This phenomenon can be explained on the base of the offered silver halide T-crystals formation mechanism⁶. The transformation of "nucleus" into a T-crystal on the diffusion mechanism during a physical ripening is the first stage. The reducing iodide ion's concentration in a T-crystal central part is caused the most probable by higher solubility of silver bromide and prevailing of bromide ions in reaction solution. As a result the bromide ions participate in growth on the diffusion mechanism mainly.

Growth of T-crystals

In the most simple case, when the fine emulsion physical ripening will be carried out in presence of bromide ions excess, the change of a ripening conditions does not influence to the T-crystals dispersion characteristics and shape, and adjusts only the duration of T-crystals formation process⁷. The resulting emulsion usually contains T-crystals both triangular, and hexagonal shape. In these conditions T-crystals size and shape distribution is determined only by conditions of fine emulsion synthesis².

Logically to assume, that the distinction on properties, resulting to T-crystals formation of one or another shape, is available already for T-crystals "nuclei". However an opportunity to operate the T-crystals shapes by varying of fine emulsions physical ripening conditions is available.

For example, if to carry out a ripening at the presence of potassium thiocyanate and at pBr value little then 2.0, the final emulsion will contain a usual T-crystals with various shapes. However if the physical ripening will be carried out at pBr value more then 2.0, essential changes are observed. Among T-crystals received in these conditions T-crystals of the hexagonal shape prevail⁸. The share of hexagonal crystals can yet be increased, if to carry out a physical ripening at the high pH value, or at the presence of some surface-active agent. The similar effect was received at realization of a fine emulsion physical ripening at the presence of TAI¹⁰. It is necessary to note, that the precise tendency to transformation of triangular T-crystals to hexagonal ones is observed at silver bromoiodide lateral shells growth on silver bromide core T-crystals¹¹, while the silver bromide lateral shells growth in the same ripening conditions does not result in essential change of shapes distribution.

In our opinion the general reason, causing hexagonal T-crystals formation in all these cases is relative

retardation of growth by diffusion mechanism. Such retardation can be caused by increase of gelatin retarding action at pH increase, or presence of the stabilizer, such, as TAI, or reduction of a silver halide solubility, as in case of silver bromoiodide lateral shell growth. The similar process can be caused by presence of some surface-active agents, which can be adsorb by a silver halide surface. The not adsorbing on silver halide surface-active agents (for example "Carbowax") do not influence on the T-crystals shapes.

Presence of modifiers results in that the growth rates of T-crystals separate lateral sides become equal. By other words, advantage in growth rate of separate sides, resulting to triangular T-crystals formation, disappears. It is possible to show, that there is the fast transformation all T-crystals without exception to correct hexagons in conditions of separate side's growth rates equalization.

On the other hand, it is known, that at lateral shells growth by fine emulsions physical ripening the essential influence can render the fine emulsions microcrystals size⁷ (Figure 3). So, the formation of identical shells on all core T-crystals is observed by use of silver bromide fine emulsion with the average microcrystals size 50 nanometers. In this case the shapes distribution between triangular and hexagonal crystals remains practically constant. If the size of fine emulsion microcrystals to increase up to 90 nanometers, there are the essential changes. First of all, a process of T-crystals majority growth is sharply slowed down. However on thicker T-crystals the lateral shell formation occurs with high former speed and the overwhelming majority of such crystals gets the form of correct hexagons.

A conclusion was made on the basis of the this phenomena that the mass transfer at silver halide T-crystals growth comes true, at least, on two mechanisms: diffusion through a solution and coalescent. The growth on the diffusion mechanism depends on a crystallographic type of surfaces, forming T-crystals lateral side. Therefore both triangular, and hexagonal T-crystals are formed at prevalence of growth on the diffusion mechanism depending on a type of T-crystals "nuclei". The coalescent mechanism of T-crystals growth becomes determining in case of ionic growth retarding (including the decrease of a solubility of fine emulsion microcrystals at increase of their size). The growth rate on the coalescent mechanism does not depend on crystallographic peculiarities of lateral sides of T-crystals and hexagonal T-crystals form irrespective of a "nuclei" type.

However the large importance gets geometrical conformity of growing lateral side of T-crystals and fine emulsion microcrystals in case of growth on the coalescent mechanism. The growth on the coalescent mechanism becomes impossible at absence of this conformity. The presence of a isometric microcrystals plenty is frequently observed in conditions of strong

retarding of ionic growth and this crystals do not built in growing T-crystals even at a long physical ripening.

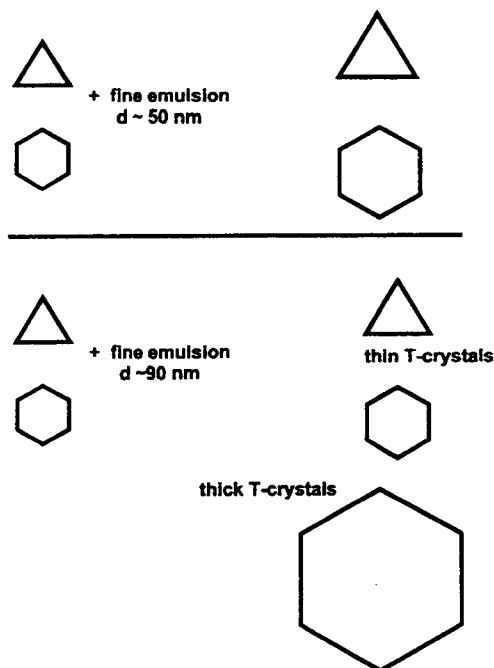


Figure 3. Influence of fine emulsion crystals size on shape and size distribution of resulting T-crystals.

The dissolution of remaining isometric crystals can be carried out, if to remove effect of retarding. But the growth of T-crystals separate sides will again proceed with different speed, and a result emulsion, containing non-uniform on size and shape T-crystals, will be received.

The additional information can give research of T-crystals, received in result of a physical ripening of the mix of silver bromide and silver bromiodide fine emulsions. A method of a "differential dissolution" allows to reveal peculiarities of silver iodide distribution in similar crystals. It is possible to see, that the areas, with the minimum silver iodide contents, are connected to directions from center of a T-crystal to its corners. Large non-uniformity of silver iodide distribution in the T-crystal is observed also. Presence of the specified peculiarities of distribution of halide structure allows to make a conclusion about peculiarities of T-crystals growth process.

Coalescent growth

This mechanism includes stage of direct contact between a microcrystal of initial fine emulsion and growing T-crystal side face and stage of recrystallization with high speed (owing to large distinction in the size). The recrystallization results to "spreading" of a fine emulsion microcrystal on a T-crystal side face. The coalescent growth is caused by process of T-crystals ionic growth.

The presence of a concentration gradient at a T-crystal surface growing side face initiates a dissolution of a fine emulsion microcrystal, that is a beginning of recrystallization process.

Geometrical conformity of a fine emulsion microcrystal and of a T-crystal lateral side is necessary, otherwise the process of a coalescence becomes impossible. It can be caused by small distinction in a solubility of a microcrystal of fine emulsion and lateral surface of a T-crystal or other reasons. This conclusion proves to be true by known results of Maskasky on ledges growing on T-crystals side faces¹². The growth of ledges proceeds only for non-blocked sides and only at presence of geometrical conformity, if the size of fine emulsion microcrystals is less than 20 nanometers.

It is obvious, that not each contact of a microcrystal of fine emulsion results in it including in a growing T-crystal. Certain time interval is necessary for the beginning of that recrystallization process realization. If the duration of contact will be less, than this time interval, the coalescence will not take place. By other words, the process of a coalescence is probability, as against of coagulation process.

Ionic growth.

If the growth of a T-crystal occurred only on the coalescent mechanism, T-crystals as disks would be probably formed. The correct geometrical structure of T-crystals is caused by the contribution of the ionic mechanism. Experimental date allow to estimate the contribution both ionic and coalescent mechanism in a general picture of T-crystals growth.

First of all the ionic growth is initiated on corners of T-crystals. Indirectly it proves to that circumstance, what sites with minimum silver iodide concentration are connected with corners. By other words the corners of T-crystals are degenerated non-equilibrium and fast-growing lateral sides of T-crystals (Figure 6). Initiation of growth on corners then results in distribution growth steps along side faces of a T-crystal.

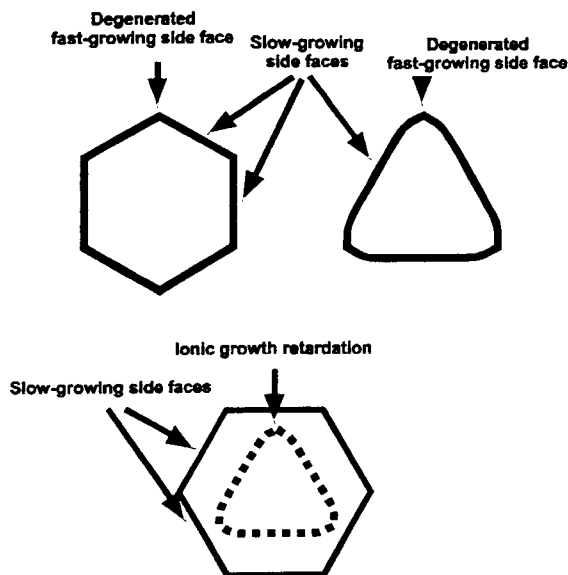


Figure 6. Localization of fast-growing and slow-growing side faces in T-crystals.

If all lateral sides of T-crystals would be identical, all T-crystals would have the shape of hexagons. However the real situation a little bit differs. We shall consider an angular part of a triangular T-crystal with large increase. It is possible to see the presence of thin structure - three corners instead of one. The main top is actually a degenerated fast-growing side face of a hexagonal T-crystal. The presence similar fast-growing side face provides higher growth rate of triangular T-crystals in comparison with hexagonal². The other two corners correspond to usual corners of a hexagonal T-crystal.

At the presence of some stabilizers (for example TAI), the growth of a triangle top is blocked (see Figure 6). The side face connected to top becomes slow-growing. The growth of sides faces, connected to corners of a hexagon thus is not blocked. Growth rates of separate T-crystals side faces is leveled and the fast transformation of a triangle into a hexagon take place. If the retarding will be removed, the distinction in growth rate of separate lateral sides again results in restoration of the former triangular form.

More precisely structure of T-crystals help to reveal known the Maskasky experiments on growing ledges on T-crystals¹². Depending on the form of initial T-crystals the picture varies rather on the strength of. For triangular T-crystals in presence bromide-TAI the most probable growth of corners appropriate to hexagon T-crystals is blocked. The growth of main triangular tops thus is not blocked and proceeds on the ionic mechanism. The growth of lateral side faces with entering structure is not blocked too. However so the initiation on a corner is impossible, the initiation occurs directly on a lateral side face. It causes selective growth on the ionic and coalescent mechanism only of this non-equilibrium side faces and formation of a ledge. The information about retarding action of TAI and bromide-TAI allow make a

conclusion about a probably structure of side faces, connected with hexagonal and triangular T-crystals corners (Figure 8).

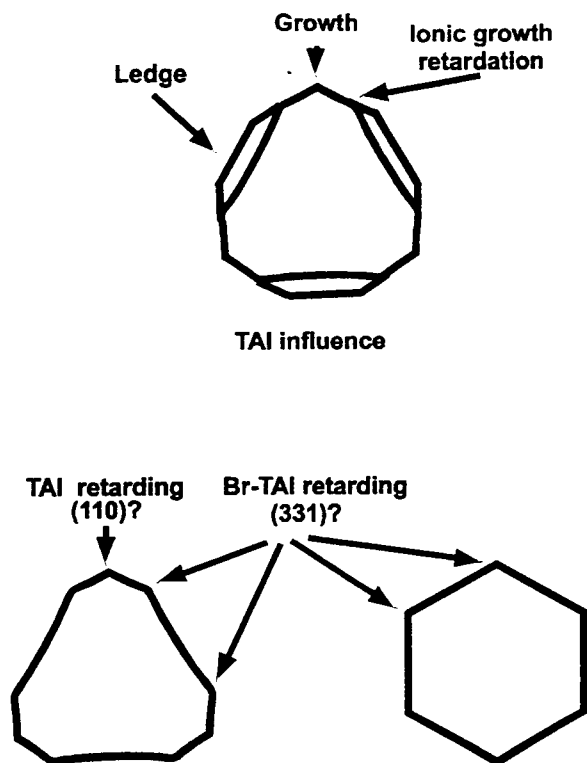


Figure 8. Influence of some stabilizers on T-crystals separate side faces growth.

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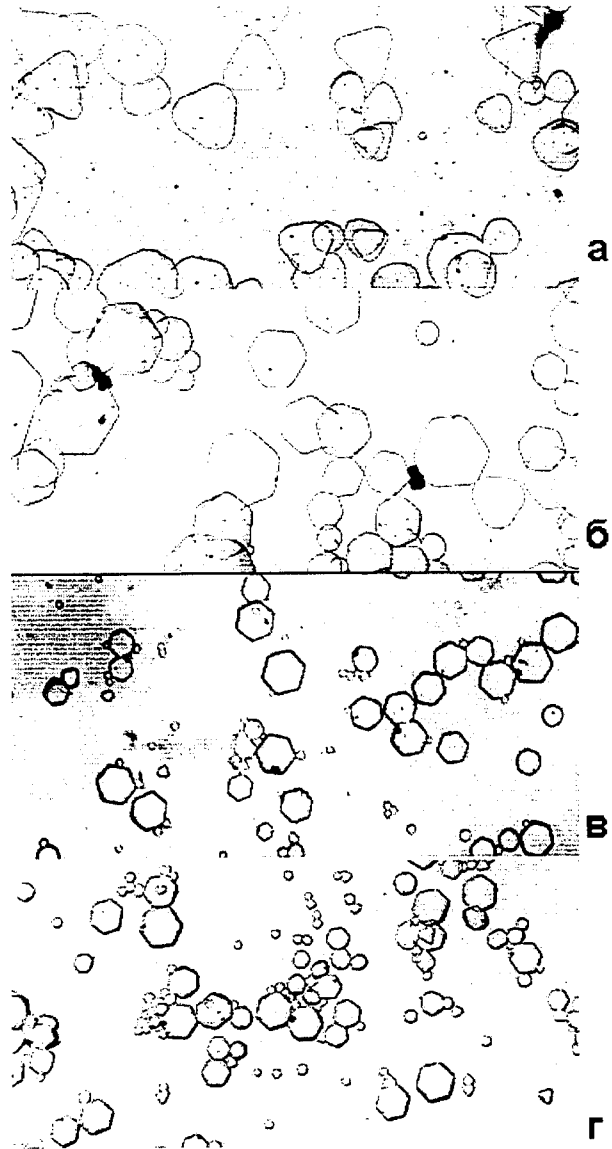


Figure 2. Microphotographs of carbonic replicas of emulsion AgBr T-crystals ($\times 6000$). The fine emulsion physical ripening conditions are:

- a - $pBr=1.1$;
- b - $pBr=2.5$, $[KSCN]=0.04 \text{ mol/l}$, $pH=6.0$;
- c - $pBr=2.5$, $[KSCN]=0.04 \text{ mol/l}$, $pH=10.0$;
- d - $pBr=2.5$, $[KSCN]=0.04 \text{ mol/l}$, $pH=6.0$, $[SV-105]=1\%$.

Figure 7. Carbonic replica microphotograph of triangular T-crystals corner ($\times 12000$).



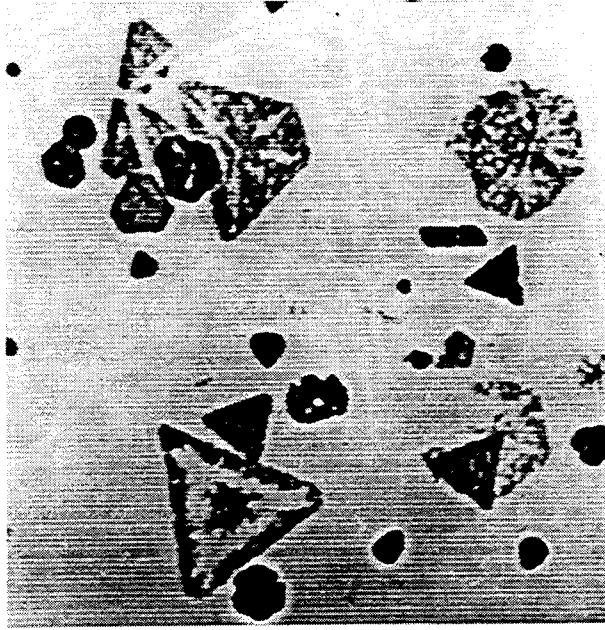


Figure 4. Microphotograph of created by mix of AgBr and AgBr_{0.96I0.04} fine emulsions physical ripening T-crystals after "differential dissolution" ($\times 1600$).



Figure 5. The coalescent growth stages.