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NASA CR.
150984

SC583.62FR August 31, 1976

EXPERIMENT MA-028 CRYSTAL GROWTH

Final Report

March 1, 1974 thru August 31, 1976

General Order No. 583
Contract No. NAS9-14015

Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Lyndon B. Johnson Space Center
Houston, Texas 77058

(NASA-CR-150984) EXPERIMENT MA-028 CRYSTAL GROWTH Final Report, 1 Mar. 1974 - 31 Aug. 1976 (Rockwell International Corp., Thousand Oaks) 22 p HC $3.50 CSCL 20B

N76-33058

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SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER

4. TITLE *(and Subtitle)*

EXPERIMENT MA-028 CRYSTAL GROWTH
ASTP FINAL REPORT

5. TYPE OF REPORT & PERIOD COVERED

Final Report
03/01/74 - 8/31/76

6. PERFORMING ORG. REPORT NUMBER

SC583.62FR

7. AUTHOR(s)

M. David Lind, Principal Investigator

8. CONTRACT OR GRANT NUMBER(s)

NAS9-14015

9. PERFORMING ORGANIZATION NAME AND ADDRESS

Rockwell International/Science Center
1049 Camino Dos Rios
Thousand Oaks, California 91360

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS

National Aeronautics and Space Administration
Lyndon B. Johnson Space Center
Houston, Texas 77058

12. REPORT DATE

August 31, 1976

13. NUMBER OF PAGES

22

14. MONITORING AGENCY NAME & ADDRESS *(if different from Controlling Office)*

15. SECURITY CLASS. *(of this report)*

Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

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17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

18. SUPPLEMENTARY NOTES

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

Crystal growth, single crystals, low gravity, experiment, calcium tartrate, calcium carbonate, lead sulfide, aqueous solutions, diffusion, Apollo-Soyuz Test Project.

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

The Crystal Growth Experiment assessed a novel process for growing single crystals of insoluble substances by allowing two or more reactant solutions to diffuse toward each other through a region of pure solvent in zero gravity. The experiment was entirely successful and yielded crystals of about the expected size, quality, and number.

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29. CRYSTAL GROWTH

EXPERIMENT MA-028

M. D. Lind[a]

ABSTRACT

The Crystal Growth Experiment assessed a novel process for growing single crystals of insoluble substances by allowing two or more reactant solutions to diffuse toward each other through a region of pure solvent in zero g. The experiment was entirely successful and yielded crystals of about the expected size, quality, and number.

INTRODUCTION

The objective of this experiment was to investigate the growth of single crystals of insoluble substances by a process in which two or more reactant solutions are allowed to diffuse toward each other through a region of pure solvent. This is a novel method of crystal growth conceived for orbital space flights to take advantage of the absence of gravity-driven convection that, on Earth, predominates over diffusion as a mechanism of material transport. The experiment performed during the Apollo-Soyuz Test Project (ASTP) mission was designed both as a first attempt to determine the feasibility of the method and as a starting point for further development.

BASIC THEORY

Because the method of crystal growth used for this experiment is closely related to gel methods of crystal growth, it is appropriate to present a brief

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review of gel methods. Gel methods are particularly applicable to the growth of crystals that have very small solubility in the solvent (usually water) that is used. In these methods, two or more reactant solutions, separated by a gel, diffuse slowly together and react according to a chemical equation of the following type as the crystal grows:

$$A \text{ (soluble)} + B \text{ (soluble)} + \ldots \rightleftarrows C\downarrow \text{ (slightly soluble)} + D \text{ (soluble)} + \ldots$$

The three reactions chosen for experiments on the ASTP flight are examples of this type reaction.

Calcium tartrate: $CaCl_2 + NaHC_4H_4O_6 + 4H_2O \rightleftarrows CaC_4H_4O_6 \cdot 4H_2O\downarrow + NaCl + HCl$

Calcium carbonate: $CaCl_2 + (NH_4)_2CO_3 \rightleftarrows CaCO_3\downarrow + 2NH_4Cl$

Lead sulfide: $PbCl_2 + CH_3CSNH_2 + H_2O \rightleftarrows PbS\downarrow + CH_3CONH_2 + 2HCl$

Typical experimental arrangements for gel methods are shown schematically in figure 29-1. In the U-tube arrangement, the crystals normally grow within the gel or at the interfaces with the reactant solutions. In the second arrangement, the crystals can grow in the pure solvent at the center.

The primary functions of the gel are suppression of gravity-driven convection and support of the growing crystal. Diffusion is the predominant mechanism for mixing of the reactant solutions. The crystal grows in a cell of solution, is exposed to the solution on all sides, and has no contact with container surfaces except those of the flexible gel structure.

The hypothesis for this experiment was based on the assumption that, in an environment of sufficiently low gravity, convection and sedimentation become negligible. Therefore, the gel is not needed for suppressing these processes and can be replaced by a region of pure solvent. Diffusion becomes the predominant mixing mechanism even with no gel present.

The advantage of allowing diffusion to be the predominant mechanism for material transport, whether in gel processes on Earth or in low-gravity processes in space flights, is that the rate of transport can be controlled by varying the concentrations of the diffusing substances and the length of the diffusion path. This is important because the rate of material transport must be compatible with the rate of crystal growth, which may also depend on other kinetic or heat-transfer factors. A diffusion-controlled process can result in better crystal quality through better prediction and control of the parameters involved. It can also result in a better understanding of crystal growth processes through simplification of theoretical treatments and a clearer comparison of the experiment with the theory.

The gel methods of crystal growth, like most aqueous solution growth methods, are advantageous because crystal growth occurs at ambient (room or spacecraft) temperature. This minimizes problems of thermally or mechanically induced strain, phase transformations, volatility of components, contamination by the container, etc., often inherent in high-temperature growth methods. However, gel methods also have certain disadvantages, including excessive nucleation that results in small crystal sizes, contamination of the crystals by gel constituents or impurities in the gel, and gel instability. The method used for this experiment is expected to overcome all these disadvantages while retaining the advantages.

Much research has been done concerning gel methods of crystal growth. This research has provided much of the background for the design of the ASTP experiment. Information particularly relevant to this experiment can be found in references 29-1 to 29-12. The three crystals (calcium tartrate, calcium carbonate, and lead sulfide) investigated in the ASTP experiments were chosen for the following reasons:

1. They are easy to grow in gel systems.
2. There has been much investigation of their growth in gel systems so that growth conditions are well known, and terrestrial results are readily available for comparison with ASTP results.
3. Calcium tartrate has been an especially important subject for investigations of gel growth mechanisms.
4. Calcium carbonate and lead sulfide have technological importance.
5. Calcium carbonate is a typical example of crystals that are contaminated by gel constituents and therefore can be improved by growth without the gel.

The experimental conditions for the ASTP experiments were based on results of previous gel growth experiments. It was assumed that the diffusion and crystal growth processes would not be very different if the gel was replaced by a region of pure solvent. Because typical gels are 95 to 96 percent solvent and only 4 to 5 percent solid, this assumption was reasonable and appears to have been validated by the ASTP results. To simplify the ASTP experimental apparatus, the usual requirement for precise temperature control was eliminated by choosing crystals that can be grown at ambient temperature without precise temperature control. The other important experimental parameters are selection and concentrations of reactant solutions, reactor dimensions, and hydrogen-ion concentration (pH) of the growth medium (water). The values of these parameters used in the ASTP experiments are summarized in table 29-I.

As previously implied, much of the behavior of these crystal growth systems could be calculated from known laws of thermodynamics, diffusion, and heat transfer. In general, the required parameters, including equilibrium solubilities as functions of temperature and pH, heats and entropies of fusion, specific heats, diffusion coefficients, thermal conductivity coefficients, etc., were reasonably well known or could be determined in experiments on Earth. However, relationships between supersaturation and nucleation are more difficult to understand, and incomplete knowledge in this area precludes a complete prediction of the behavior of the crystal growth systems chosen for study. Consequently, it was necessary to estimate the best growth conditions on the basis of results of experimental gel growth studies.

EQUIPMENT

The experimental apparatus consisted of six specially designed and fabricated reactors (fig. 29-2). The entire set of flight hardware is illustrated in figure 29-3. Each reactor had three compartments that were separated by valves operated by the knobs at each end. Each compartment had a separate filling port. The compartments varied in length, as indicated in table 29-I. The reactor covers were flat and transparent to permit photographing the progress of diffusion and crystal growth. The reactors were constructed of Lexan polycarbonate resin with silicone rubber gaskets and seals, porous high-density polyethylene diaphragms between the compartments, and aluminum knobs.

Before delivery of the hardware to the launch facility, the reactors (with the intercompartment valves in the closed positions) were filled with the various solutions. The reactant solutions were placed in the outer compartments of each reactor, and the central compartment was filled with water.

The six reactors were mounted in the U-4 locker in the command module. They were accessible in this location, yet out of the way of other operations.

After the joint phase of the flight, at approximately 109 hours ground elapsed time (GET), a crewman activated the experiments by opening the intercompartment valves to allow the reactants to begin diffusing toward the center. A wrench (fig. 29-3) that was included as a contingency measure was not required.

Beginning at the time of activation and at approximately 12-hour intervals for the remainder (116 hours) of the flight, a crewman took color photographs of the six reactors with the Nikon 35-mm camera used for various other photography. A framing device designed and fabricated at the NASA Lyndon B. Johnson Space Center was used to place the camera properly.

Throughout the flight, the experiment progressed as planned with no problems or anomalies. The performance of the reactors was most satisfactory. There was no evidence of leakage through the intercompartment valves before activation of the experiment, and the valves were opened easily at the proper time to begin the experiment. Photographs of the reactors taken during the flight are of excellent quality and verify that the framing device, camera settings, and lighting were entirely satisfactory.

DISCUSSION AND RESULTS

Crystals of about the expected size, quality, and number formed in all six reactors. Experiment results are shown in figures 29-4 to 29-6, which are photographs taken after return of the reactors to the laboratory. Upon receipt of the reactors and before opening them, the reactors and their contents were examined visually through the reactor faces with a binocular polarizing microscope of 40× magnification. The reactors were photographed with 1.5× magnification, and representative crystals were photographed through the reactor faces with 10× magnification. Following this procedure, representative crystals were removed through the center fill ports for further examination. The identity of each kind of crystal was confirmed by single crystal X-ray diffraction data obtained with Buerger precession and Gandolfi cameras. As expected, the X-ray diffraction data are identical with those of Earth-grown crystals. For several calcium tartrate crystals, X-ray diffraction topographs were obtained with a Lang camera for comparison with those of Earth-grown crystals. To date, these comparisons indicate about equal crystal quality.

The best crystals obtained were the calcium tartrate crystals (fig. 29-4). This result was not surprising because these crystals are among the easiest to grow by gel methods. Both calcium tartrate reactors produced numerous prismatic crystals with maximum dimensions as large as 2 mm and platelike crystals as long as 5 mm; these crystals have good face development, are very clear, and appear flawless when viewed in the microscope both with unpolarized light and with light transmitted through crossed polarizers. The quality of these crystals is confirmed by X-ray diffraction topographs. There were also a few platelike crystals as long as 10 mm but of somewhat poorer quality. The absence of finely divided precipitate indicated that mixing of the reactant solutions and crystal growth were complete by the time of spacecraft reentry, which was the desired result. Contrary to the experience with gel experiments, the platelike crystals were more numerous and larger than the prismatic crystals. Platelike crystals have been obtained occasionally in gel experiments, but the prismatic habit is more usual. The reasons for this variation in habit and its significance are unknown at this time.

Each of the two calcium carbonate reactors produced numerous well-formed clear rhombohedral crystals as long as 0.5 mm on an edge (fig. 29-5). These crystals are very similar in appearance to Earth-grown calcium carbonate crystals, both synthetic and natural. Although small, they are large enough to exhibit birefringence. Again, no finely divided precipitate resulted, which indicates that, as desired, mixing of the reactant solutions and crystal growth were complete by the time of spacecraft reentry. Most of the calcium carbonate crystals adhered to the reactor, which implies that/ for $CaCO_3$ growth the polycarbonate material is not the best surface for the interior walls of the reactors.

The two lead sulfide experiments were less successful, but both resulted in the production of discrete single crystals with dimensions as large as 0.1 mm (fig. 29-6). In this case, the mixing and reaction were not complete at the time of reentry. A fine precipitate was observed that continued to increase even after return of the reactors to the laboratory. This result indicates that a longer time is needed for successful growth of larger lead sulfide crystals under the conditions used. An alternative way of obtaining better results is to use a somewhat higher temperature to increase the solubility of one of the reactants (lead chloride).

The calcium carbonate crystals are easily visible in the series of photographs taken at 170 hours GET (61 hours after activation of the experiment) and are increasingly visible in subsequent photographs. Representative photographs are shown in figure 29-7. A small number of calcium tartrate crystals also appear in these photographs, but less clearly. The photographs indicate that most of the calcium tartrate crystals must have grown after the last series of photographs was taken. The flight continued for more than 6 hours after the last series of photographs; therefore, it is quite possible that substantial growth occurred after that time. It is very likely that the calcium tartrate crystal growth was complete before reentry, because virtually all the calcium tartrate crystals were free of the reactor walls as if they were grown in low gravity. Repeated experiments in normal gravity have shown that rapid mixing in one-g will result in a much smaller particle size and that the crystals thus formed adhere to the bottom of the reactor. It is reasonable to assume that reactant concentrations were just reaching the values required for calcium tartrate growth at the end of the flight. It was also observed that some additional calcium carbonate crystals grew after the last series of photographs was taken.

The photographs also provide a record of the movement of air bubbles in the reactors during the flight. The air bubbles migrated from the expansion spaces in the fill-port caps during handling of the reactors before flight. It would have been preferable to avoid the presence of the bubbles, but they apparently did not have any significant negative effect on the experiment. In fact, their presence allowed the beneficial effect of a rough evaluation of the accelerations experienced by the reactors. It is interesting to observe that air bubbles in the two calcium tartrate reactors remained stationary throughout the flight. Bubbles in the calcium carbonate and lead sulfide reactors were more mobile but remained stationary for as long as the 12-hour interval between photographs. The difference in mobility of bubbles in the various reactors is not understood; however, movement of the bubbles shows that accelerations experienced by the reactors during the flight were small.

During the flight, the cabin temperature varied more than had been anticipated and more than was desirable for crystal growth from solutions. The cabin temperature ranged between approximately 297 K (75° F) and approximately 289 K (60° F) during the flight. Solubilities of the reactants and crystalline products are strongly dependent on temperature, and the temperature variations were sufficient to markedly affect the results of this experiment. Such large temperature variations were not expected when the decision was made to neglect temperature control to simplify the experimental hardware.

The crystals grown during the flight are at least as good in size, quality, and number as those obtained by gel methods on Earth in the same length of time. Nucleation was excessive in all six reactors, which indicates the need for considerable refinement of the experimental parameters to suppress nucleation and improve crystal size and quality. Precise temperature control and longer growth times are probably the two main improvements to be made.

SUMMARY

Results of the Apollo-Soyuz Crystal Growth Experiment successfully proved the feasibility of this novel method of crystal growth and indicate that the method, with further refinement, should yield superior crystals of a variety of materials. It still appears likely that conditions can be optimized to produce larger crystals than can be obtained with gels. High purity remains a major potential advantage of this method. Because of its simplicity, the method should also promote a better understanding of crystal growth theory.

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TABLE 29-I.- REACTANT SOLUTIONS

Reactor serial number	Compartment B		Compartment A		Compartment C	
	Reactant	Length, cm	Reactant	Length, cm	Reactant	Length, cm
005	0.1M CH_3CSNH_2	3.30	H_2O adjusted to pH = 1.0 with HCl	5.08	Saturated $PbCl_2$	3.30
006	0.5M $CaCl_2$	3.30	H_2O	5.08	0.45M $NaHC_4H_4O_6$	3.30
[illegible]	0.5M $CaCl_2$	3.30	H_2O	5.08	0.5M $(NH_4)_2CO_3$	3.30
008	0.1M CH_3CSNH_2	3.30	H_2O adjusted to pH = 0.5 with HCl	5.08	Saturated $PbCl_2$	3.30
012	0.5M $CaCl_2$	4.19	H_2O	4.19	0.5M $(NH_4)_2CO_3$	3.30
013	0.5M $CaCl_2$	4.19	H_2O	4.19	0.45M $NaHC_4H_4O_6$	3.30

FIGURE LEGENDS

Figure 29-1.- Typical experimental arrangements for gel methods of crystal growth.

Figure 29-2.- Schematic diagram of a reactor.

Figure 29-3.- Flight hardware.

Figure 29-4.- Calcium tartrate.

(a) Serial number 006.

(b) Serial number 013.

(c) Magnified view of calcium tartrate crystals.

Figure 29-5.- Calcium carbonate.

(a) Serial number 007.

(b) Serial number 012.

(c) Magnified view of calcium carbonate crystals.

Figure 29-6.- Lead sulfide.

(a) Serial number 005.

(b) Serial number 008.

(c) Magnified view of lead sulfide crystals.

Figure 29-7.- Selected photographs of the calcium tartrate and calcium carbonate reactors taken during the flight.

(a) 170 hours GET.

(b) 218 hours GET.

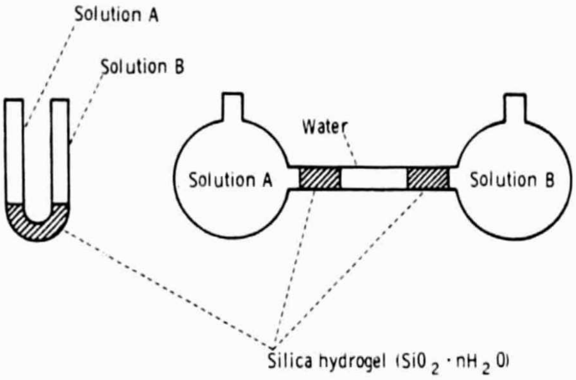


Figure 29-1. - Typical experimental arrangements for gel methods of crystal growth.

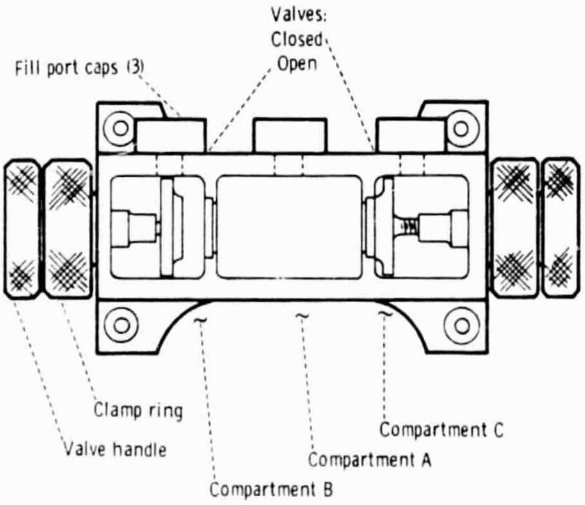
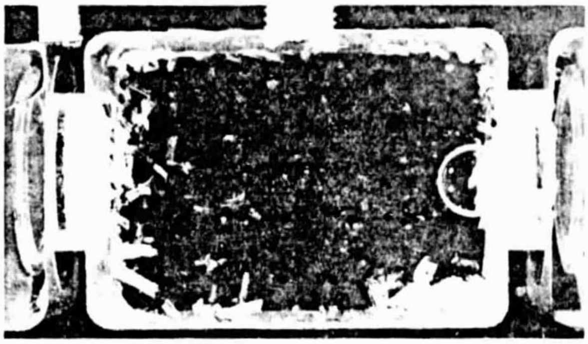
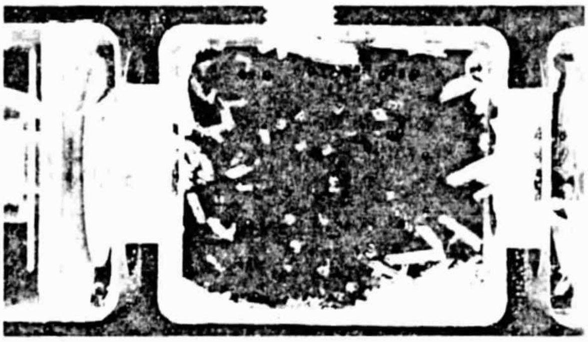


Figure 29-2. - Schematic diagram of a reactor.

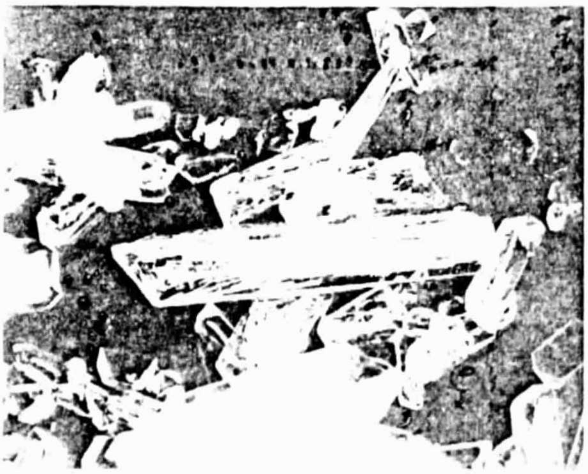
Figure 29-3. - Flight hardware.



(a) Serial number 006.



(b) Serial number 013.



(c) Magnified view of calcium tartrate crystals.

Figure 29-4. - Calcium tartrate.

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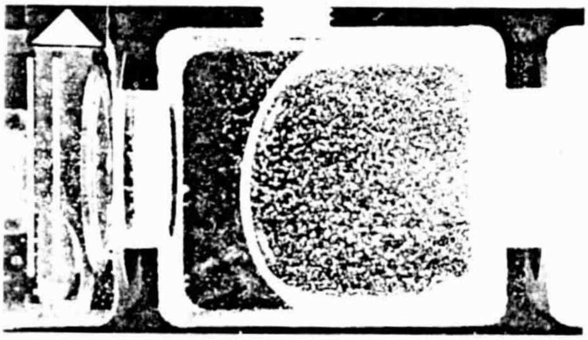
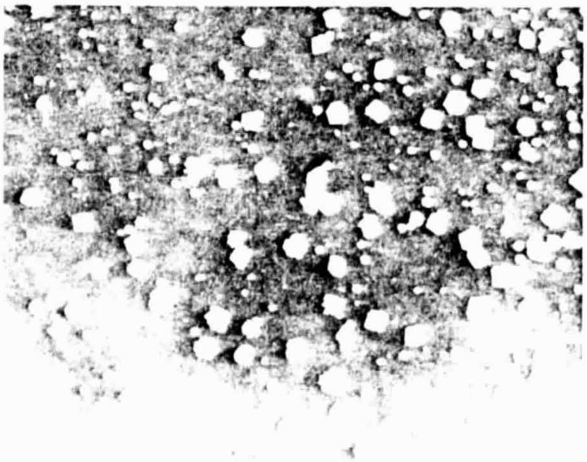
(a) Serial number 007.



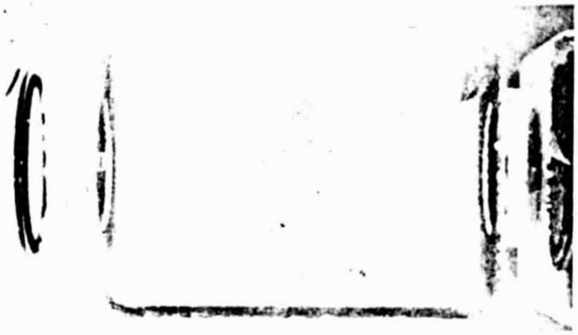
(b) Serial number 012.



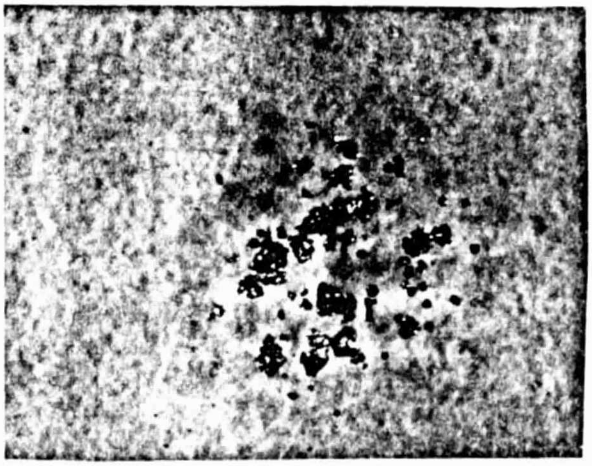
(c) Magnified view of calcium carbonate crystals.

Figure 29-5. - Calcium carbonate.

(a) Serial number 005.



(b) Serial number 008.



(c) Magnified view of lead sulfide crystals.

Figure 29-6. Lead sulfide.

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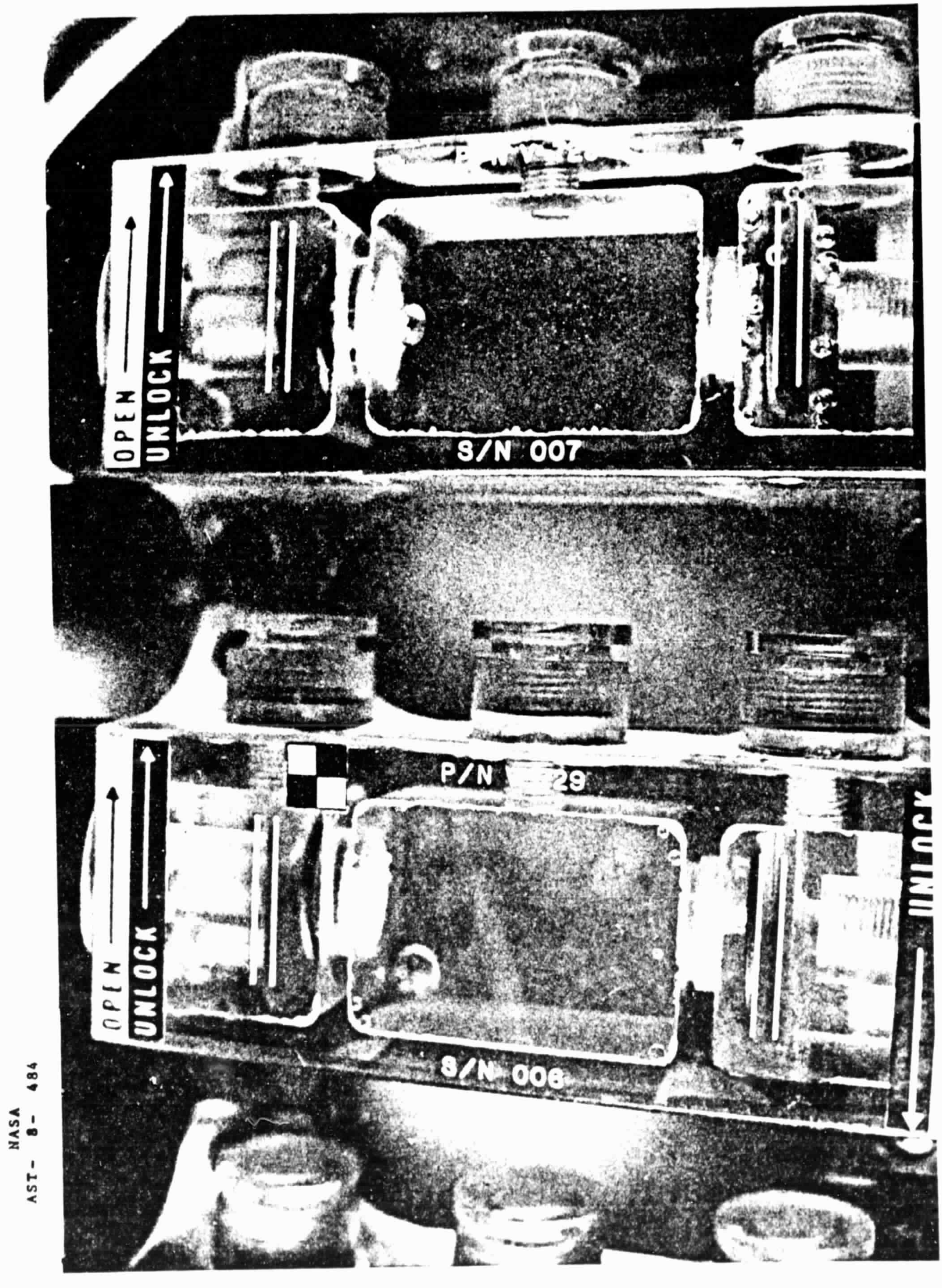
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Figure 29-7. (a)

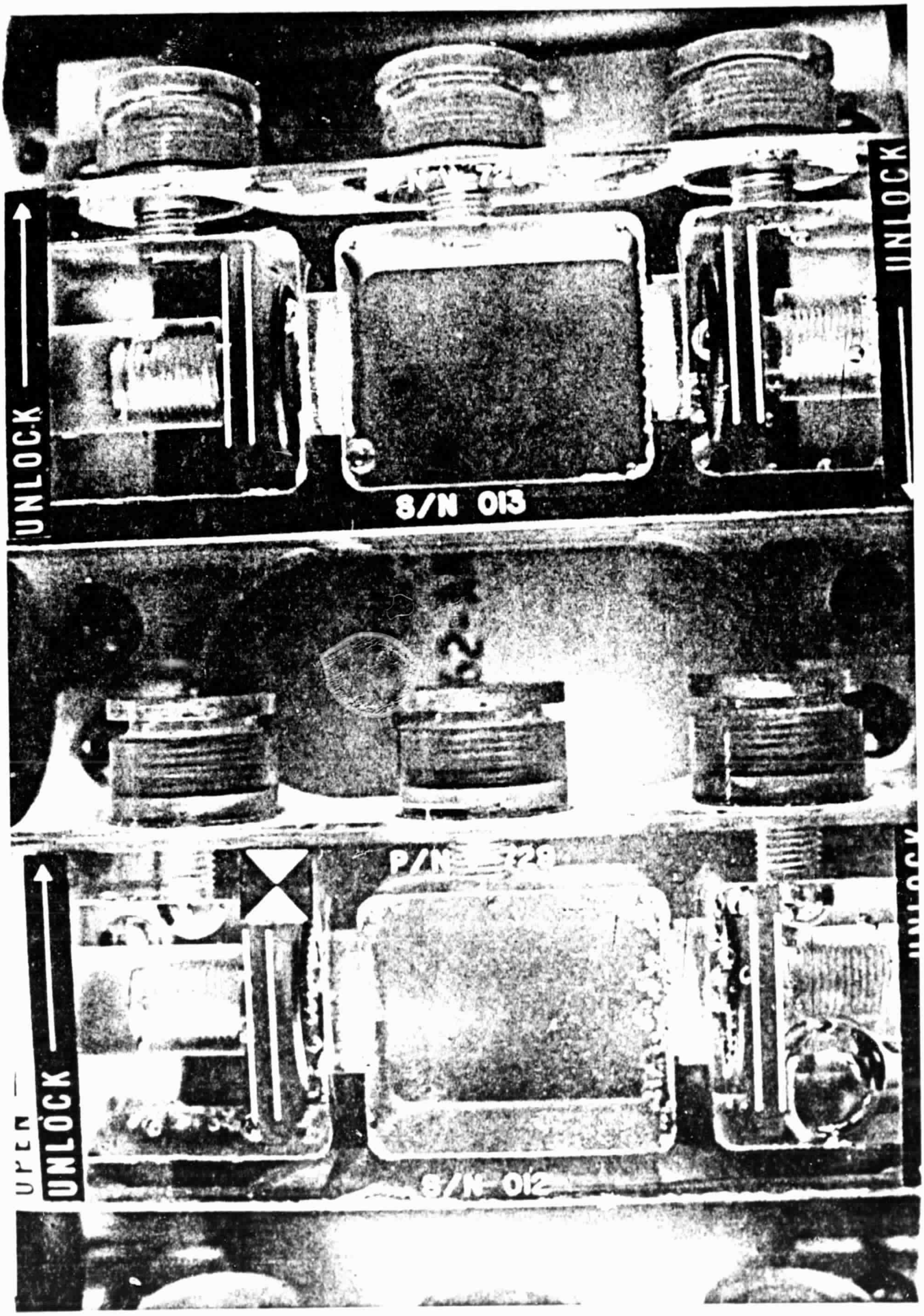

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Figure 29-7. (a)

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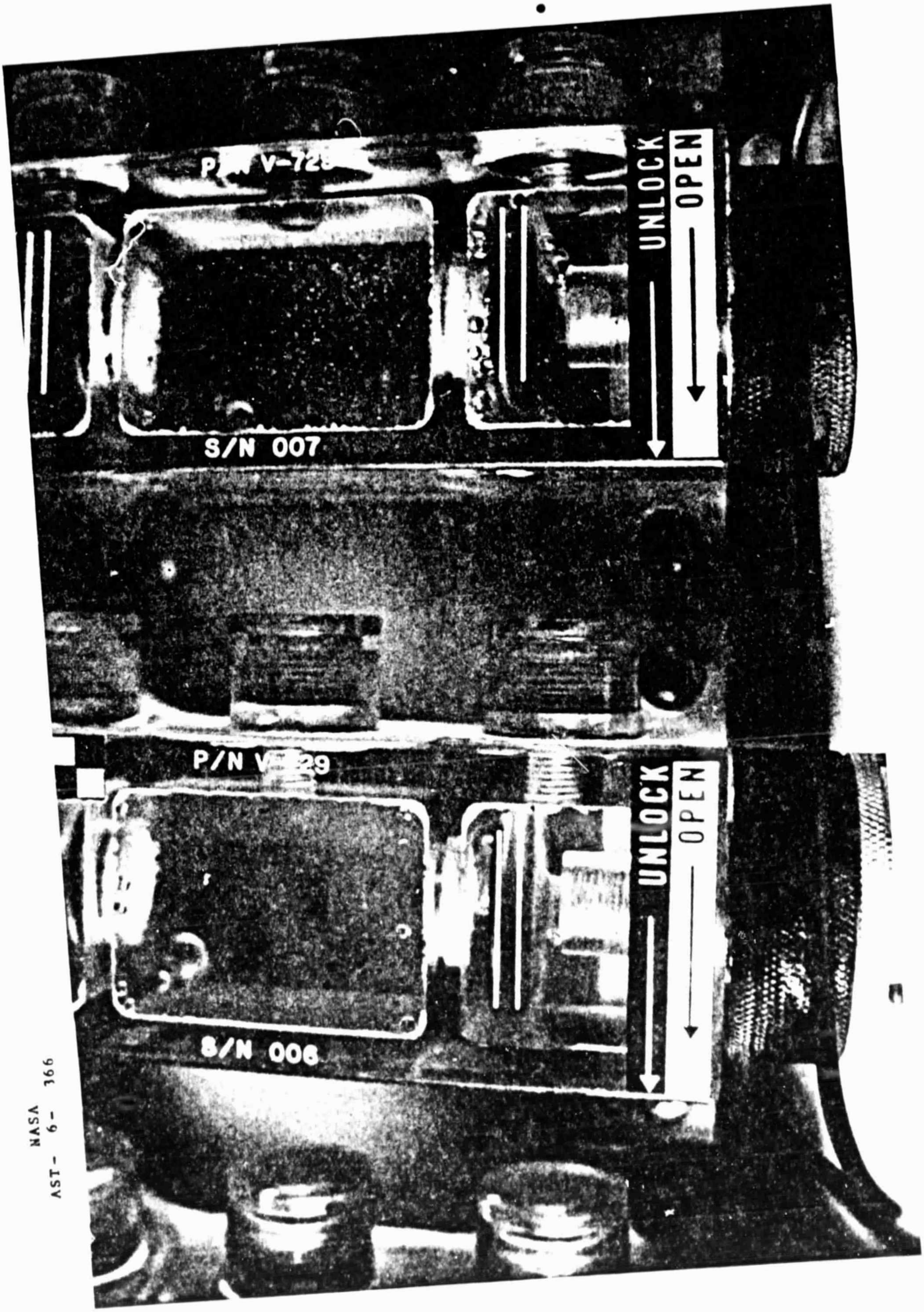

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Figure 29-7. (b)

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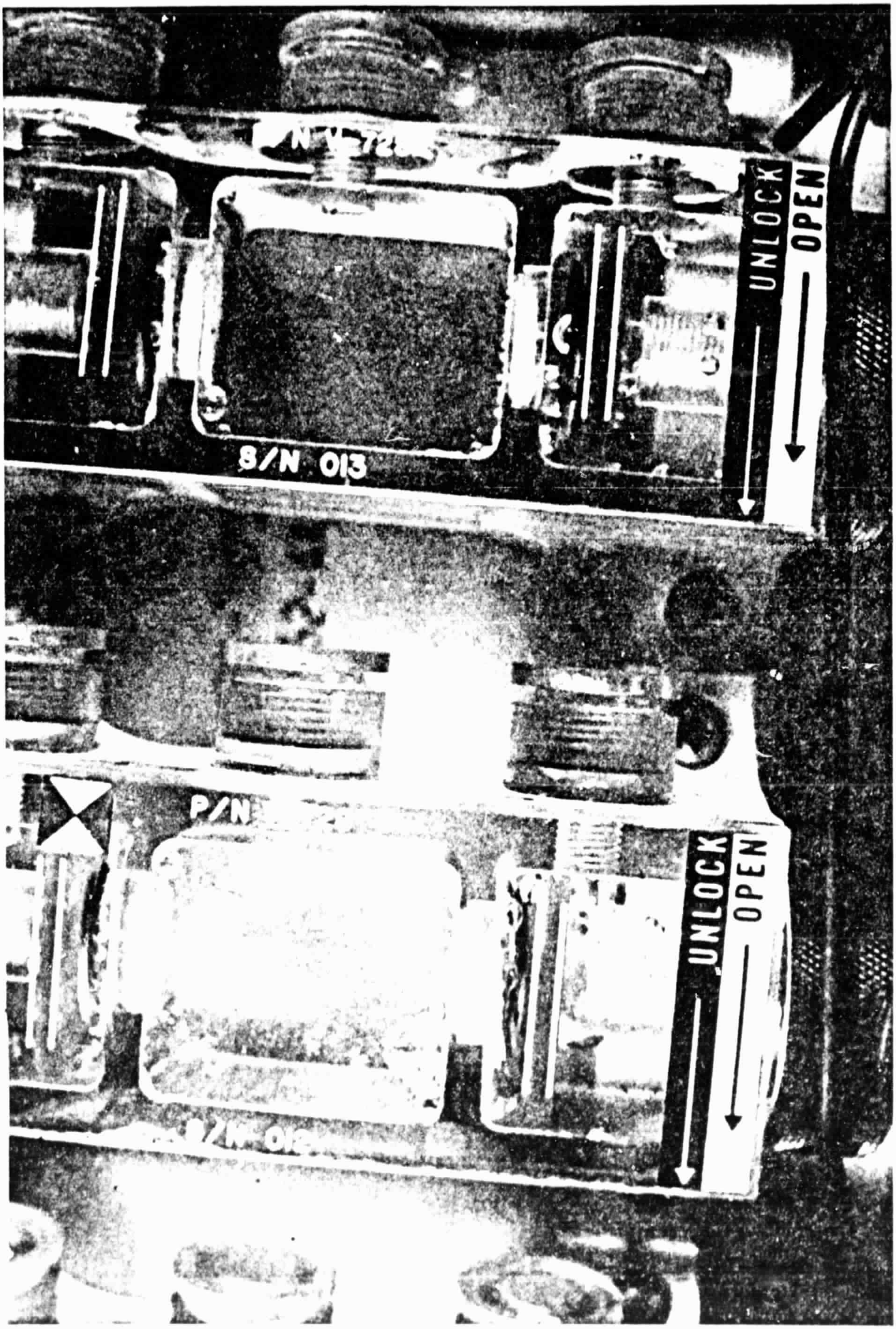

Figure 29-7. (b)

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