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**In 1982, the name of the International Superphosphate Manufacturers' Associations (ISMA) was changed to International Fertilizer Industry Association (IFA).*

STUDY OF THE MECHANISMS OF CAKING
IN SOME PRILLED NITROPHOSPHATE FERTILISERS

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SUMMARY AND CONCLUSIONS

Factors responsible for caking in prilled NP and NPK nitrophosphate fertilisers were investigated. The following observations were made :

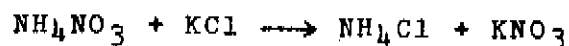
The prills are composed of coarse crystals of KCl and kieserite, and a fine crystalline composite consisting of water soluble nitrates and phosphates, together with water insoluble dicalcium and calcium fluorides.

The prills have an even, smooth surface whose crystals are optically isotropic. The surface is enriched in nitrate compared with the bulk material.

At 22° C the moisture in a product containing potassium chloride and with a water content of 0.3% is at equilibrium at 30% relative humidity. If this product is exposed to air of higher humidity, absorption of moisture takes place.

An NH_4NO_3 -rich liquid phase is formed on the surface during moisture absorption. This liquid is carried, probably by capillary forces, into the interior of the prills. This movement of the liquid results in a reduced nitrate, ammonium, potassium and chloride content in the surface layer, while the phosphate content increases.

Water absorption increases particle volume and may result in cracks. This phenomenon may be partly caused by the reaction :



since changes in chemical composition of the surface layer is less in the case of NP prills.

A dry and smooth area of contact is formed when NPK prills of low water content are pressed together. The contact surface consists mainly of sintered NH_4NO_3 crystals. The particles stick together only weakly.

If the water content of the particles is increased, relatively large and moist contact areas are formed when the prills are pressed together. Recrystallization between particles takes place when the ambient relative humidity or temperature is lowered. The recrystallization causes the particles to adhere more strongly.

Samples of NPK nitrophosphate fertilisers which have been cycled between 22°C to 40°C , have a greater tendency to caking than uncycled products.

INTRODUCTION

Caking of NPK fertilisers is related to chemical composition, water content, pressure during storage, as well as the temperature and humidity of the atmosphere.

The aim of this paper is to explain caking in terms of chemical and physical changes in the particles.

The NPK fertiliser samples used in the study were uncoated prills from our own NPK plants based on the Odda-process.

In the Odda-process, the rock phosphate is first dissolved in nitric acid. From the resulting solution the calcium content is partly removed as $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ by crystallization and separation. The mother liquor is neutralized with ammonia. The neutral suspension contains ammonium nitrate, ammonium phosphates, dicalcium phosphate and impurities. The water content is reduced by evaporation. The final suspension is then mixed with potassium chloride and any other required components. The mixture is then granulated or prilled.

At the time of these experiments the water solubility of the phosphate in the fertilisers was about 50%. The plants were subsequently converted to the deep cooling process, which yields products of about 80% water soluble phosphate. The conclusions are believed to be valid for these products also.

EXPERIMENTAL

Microscopy examination

a) Sample composition

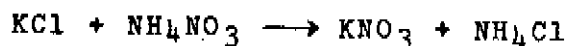
The samples contain mono- and diammonium phosphates, dicalcium phosphates, ammonium nitrate, potassium salts (chloride or sulphate), magnesium sulphate and small amounts of impurities. In the following text the nutrient content of the samples is expressed as percentages of elemental N, P and K.

b) Internal structure

Prills of NPK 16-5-12 (with KCl) were mounted in self-curing polyester and sliced by means of a microtome.

The samples were examined by microscope using direct light beam equipment and optical magnification.

The examination, see Figures 1, 2 and 27, showed that the prills are composed of coarse $MgSO_4 \cdot H_2O$ (kieserite) and KCl crystals enveloped in fine crystalline material. According to crystal optical examination, the fine crystals contain NH_4Cl and KNO_3 . On the contact surface between the coarse and fine crystals there is a layer which is most probably formed according to the reaction :



In newly produced prills of low water content, the degree of KCl conversion is low. The conversion increases with increasing water content of the product.

The observed kieserite crystals exhibit high gloss crystal planes with sharp edges, which implies that these crystals, at least initially, are not an actively reacting component.

c) Surface structure

From visual inspection, NPK prills have a smooth and even surface. A typical example is shown in Figure 3.

The surface of an NPK 16-5-12 containing about 0.3% H_2O is shown in Figure 4.

Examination by polarised light shows an isotropic surface which indicates that the outer shell consists of super-cooled melt, or a solid solution.

By rubbing a particle of NPK 16-5-12 containing 0.3% H_2O under slight pressure across a dry object glass in a box with air humidity below 30%, some surface material is smeared

onto the glass surface. Examination of such a sample under a microscope with phase contrast optics reveals small round spheres of CaHPO_4 and irregularly shaped particles of different composition, see Figure 5.

The irregularly shaped particles rapidly absorb moisture from air blown across the sample. The particles are eventually completely dissolved. A brief exposure in drier air, leads to the formation of dendritic crystals, see Figure 6. Some of the crystals are isotropic in polarised light while the bulk is anisotropic. The isotropic crystals consist of NH_4Cl and the anisotropic crystals mainly of NH_4NO_3 .

d) Effect of moisture on surface structure

When NPK particles are exposed to air with a higher relative humidity than the equilibrium moisture content, absorption of water takes place.

Surface changes in an NPK 16-5-12 caused by exposure to moist air have been observed under a microscope using reflected light.

Photomicrographs are shown in Figures 7, 8, 9 and 10.

Figure 7 shows part of a granule surface exposed to air with 30% relative humidity at 25° C.

Figure 8 shows the same area when exposed for 10 seconds to air of 50% relative humidity. It can be observed that changes have occurred, and irregularly shaped water droplets have formed. By further increasing exposure time to the air, to about 30 seconds, the complete surface is covered with a liquid film, see Figure 9.

Recrystallization takes place when the same particle is kept in drier air for a few minutes (35% relative humidity), while moisture is disappearing from the surface, see Figure 10.

By increasing the initial exposure time to moist air the crystals which are formed during the subsequent exposure to air of 35% relative humidity gradually become coarser. Figures 11 and 12 show the recrystallized crystals after initial exposure of 1 and 3 minutes respectively to moist air. Most probably, this effect is caused by recrystallization taking place in a thicker and less concentrated moisture film.

Initially, during the period of moisture absorption, an NH_4NO_3 -rich salt solution is formed in the surface layer. After a while the concentration of NH_4NO_3 decreases in the

surface layer and increases in the inner part of the granule. This migration is a result of capillary forces and the low water content in the centre of the granule. During the migration, the NH_4NO_3 salt solution phase passes across KCl crystals, resulting in the formation of KNO_3 and NH_4Cl . This reaction combined with water absorption leads to a volumetric increase and the formation of cracks in the particles. Figure 13 shows particles exposed to air of 50% humidity for 20 hours.

e) Effect of pressure on surface structure

In these experiments two prills of about 3 millimetres diameter were pressed together using a force of 50 grams for 10 minutes. Then the prills were carefully separated and the contact layers examined under a microscope.

Figure 14 shows an area of the surface of an NPK 14-4-17 (with KCl) before pressure treatment. The prills were exposed to air of 35% relative humidity (22°C) for a short time so that the water content increased from about 0.25% to about 0.30% before the photomicrograph was taken. Figure 15 shows the contact area after pressure against another granule.

Figure 15 shows that deformation and compaction have taken place. One can observe an almost plane contact area with a very finely grained structure. The contact surface is dry, which has probably prevented recrystallization and crystal bridge formation. We have obtained similar contact surfaces by pressing single prills against glass plates.

The effect of pressure clearly increases as the water content increases. The surface becomes softer and the area of contact increases. The structure appears to be coarser and after a while a liquid phase is formed at the area of contact. All these factors lead to stronger binding forces between contacting prills.

Figures 16 and 17 show contact areas of an NPK 14-4-17, with water contents in equilibrium respectively at 15% and 50% relative humidities at 22°C , after submission to a 50 gram pressure against glass plates. On the granules with the lower water content, there is a dry contact surface with an even structure and clear indications of sintering. On the granules with the higher water content one can observe a moist contact surface with an uneven structure.

Thus, when particles are in contact, recrystallization and crystal bridge formation may take place due to the presence of the liquid phase.

Figures 18 and 19 show the results of similar experiments using an NPK 13-5-10 (with K_2SO_4). This product is known to have a lesser tendency to caking than NPK 14-4-17, and the effect of pressure was found to be less pronounced.

In the examples discussed above the prills were exposed to moist air prior to pressurization. Experiments have also been carried out in which pressure application and water absorption took place simultaneously. These experiments were made at a 60% relative humidity at 25° C.

Figures 20 and 21 show part of the contact area of two prills of NPK 16-5-12 which have been pressed together for 10 minutes. One can observe crystals in the area of contact. Between the crystals there is a moist substance. The composition of the crystals is very probably NH_4NO_3 , although this cannot be determined with certainty.

As shown later, the surface is enriched in NH_4NO_3 . NH_4NO_3 crystals are fairly soft and can easily be pressed into compact discs, even when exposed to a pressure of only 0.5 kg/cm². A photomicrograph of an NH_4NO_3 disc surface is shown in Figure 22. When two NH_4NO_3 discs are pressed together under a pressure of about 0.5 kg/cm² it is difficult to separate them afterwards. When examined under a microscope, no break can be observed in the contact surfaces after the pressure treatment. Nor is there any sign of crystal bridge formation. A possible explanation for the strong adhesion could be the existence of a very thin, viscous film of NH_4NO_3 solution, which may have been formed because of the heat of friction and/or increased solubility of NH_4NO_3 at the higher pressures.

Similar experiments have been performed with discs of NH_4Cl , KNO_3 , $NH_4H_2PO_4$ and $(NH_4)_2HPO_4$. All these compounds are harder than NH_4NO_3 , and have to be exposed to higher pressures to yield good quality discs. When pressing together one disc of NH_4Cl and another of KNO_3 , the adhesion between the discs after 8 days pressure was very weak. None of the other disc combinations was as strong as that with NH_4NO_3 disc pairs.

The presence of the liquid phase can be demonstrated with a stereomicroscope when pressing a thin glass plate against a prill of NPK 16-5-12 with about 0.4% H_2O . Photomicrographs, see Figures 23 and 24, show interference fringes due to liquid phase contact with the glass plate. By using suitable techniques, the liquid phase has been isolated. Chemical analysis shows the main components to be NH_4^+ , NO_3^- , K^+ and Cl^- .

It has thus been shown that, when prills of low water

content are pressed together, deformation takes place only to a small extent. Ammonium nitrate crystals, enriched in the particle surface, will, when compacted, form an even and comparatively dry contact area. At constant temperature and humidity there is no formation of crystal bridges. The granules sometimes adhere weakly to each other. Prills of higher water content have softer and moister surfaces which leads to the formation of a relatively large and moist contact area. Recrystallization and the formation of firm crystal bridges due to ambient temperature and moisture variations may take place.

f) Crystal bridge composition

The chemical composition of crystal bridges is important for the understanding of what takes place during caking. Under the microscope, the binding substances were found to consist mainly of a fine crystalline mixture of KNO_3 and NH_4Cl .

Figure 25 shows a cross-section of a crystal bridge. The KCl crystal is surrounded by a shell consisting of NH_4Cl and KNO_3 . The same phenomenon is shown in Figure 26, which is a cross-section of two caked granules. The NPK 16-5-12 examined contains a number of KCl crystals in the surface of the particles, see Figure 27.

In a number of cases it has been found that the binding substance consists of very small, needle-shaped isotropic and anisotropic crystals. By means of crystal optical examination employing polarised light, NH_4 phosphates, NH_4NO_3 , NH_4Cl , KNO_3 and ball-shaped CaHPO_4 have been found. It was not possible to carry out quantitative analysis. Qualitatively, there seems to be little difference in chemical composition between the binding substance and substance from the surface of the particles. However, from a morphological point of view there is a marked difference. The crystals in the binding substance are plate or needle-shaped. The crystals from the particle surface are often dendritic. This difference shows that, in the area of contact between particles, recrystallization has taken place.

Chemical and physical examination

a) Chemical composition of prill surface

A sample of NPK 16-5-12 was taken from the bottom of the plant prilling tower to the laboratory in a Dewar-flask.

Four samples of 10 grams were shaken with quartz powder

for 20 minutes at 53° C. Another set of samples was first cooled to 20° C and then shaken with quartz. A third set was shaken in the same manner after an initial 6 days storage period at 20° C in an airtight container. The smeared quartz powder was recovered and washed with weak acid. The solution was analysed for P, Cl, NO₃-N, NH₃-N, K and Ca.

The results are given in Table 1. Only small differences are observed between the various treatment groups. The results show the composition of the surface of the particles to be the same at 20° C and 53° C. No changes occurred during the six days of storage in an airtight container.

Table 1 - COMPOSITION OF SURFACE FROM PRILLED NPK 16-5-12

| Component | 53° C | Initial cooling to 20° C | Six days storage at 20° C | Bulk product |
|-----------------|--------------------|--------------------------|---------------------------|--------------------|
| | grams/ 100 grams A | grams/ 100 grams A | grams/ 100 grams A | grams/ 100 grams A |
| PO ₄ | 7.6 | 8.1 | 7.6 | 17.4 |
| Cl | 7.8 | 7.8 | 7.3 | 14.6 |
| NO ₃ | 58.1 | 58.2 | 58.1 | 36.3 |
| NH ₃ | 16.9 | 15.8 | 16.4 | 11.4 |
| K | 8.1 | 8.3 | 8.9 | 15.0 |
| Ca | 1.5 | 1.8 | 1.7 | 5.0 |

$$A = \sum (PO_4 + Cl + NO_3 + NH_3 + K + Ca) \text{grams}$$

When comparing the mean value for each treatment group with the figures for the main NPK bulk product, one observes that the surface layer is enriched in nitrate and that the K and Cl contents are lower than with the bulk product.

b) Surface changes due to moisture absorption

Microscopic examination of NPK prills showed that considerable changes occurred in the particle surface and also in the inner parts during exposure to humid air. The more easily soluble salts on the surface were probably dissolved and carried by diffusion towards the interior of the particle. Quantitative analyses were carried out to test this hypothesis and the results are described below :

A sample of prilled NPK 14-4-17 was exposed to air (25° C, 57% relative humidity). During this period moisture was absorbed and the water content of the sample increased from 0.29 to 1.06%. Analyses of the surface layers from samples set aside during the period of water uptake are shown in Figure 28. Table 2 shows the bulk composition of the sample prior to the treatment.

Table 2

| Component | NO ₃ -N | NH ₄ -N | P | K | Cl | Ca | H ₂ O |
|------------------|--------------------|--------------------|-----|------|------|-----|------------------|
| gm/100 gm sample | 6.5 | 7.6 | 4.2 | 18.1 | 16.8 | 2.9 | 0.29 |

The results confirm the microscope observations and indicate that even a small degree of water absorption leads to marked changes in surface structure as well as in chemical composition.

Similar experiments were carried out with other product formulations, eg. NPK 13-6-15 (with KCl), NPK 12-5-15 (with K₂SO₄) and NP 20-9. The results are shown in Tables 3 to 5. The effect of water uptake on surface composition is less with an NPK fertiliser based on K₂SO₄ than with an NPK fertiliser based on KCl. In the case of an NP fertiliser the effect has practically disappeared.

Table 3 - SURFACE COMPOSITION OF NPK 13-6-15 (with KCl)

| Component | Sample containing 0.40% H ₂ O | Sample containing 0.56% H ₂ O | Sample containing 1.06% H ₂ O | Bulk composition |
|-----------------|--|--|--|-------------------|
| | grams/100 grams A | grams/100 grams A | grams/100 grams A | grams/100 grams A |
| PO ₄ | 10.2 | 17.0 | 36.5 | 19.1 |
| Cl | 14.4 | 14.9 | 8.6 | 18.0 |
| NO ₃ | 43.0 | 37.6 | 25.7 | 27.9 |
| NH ₃ | 14.4 | 15.1 | 10.9 | 9.1 |
| K | 13.8 | 10.9 | 7.3 | 19.5 |
| Ca | 3.4 | 4.8 | 10.9 | 6.4 |

$$A = \sum (PO_4 + NO_3 + NH_3 + K + Ca + Cl) \text{ grams}$$

Table 4 - SURFACE COMPOSITION OF NPK 12-5-15 (with K₂SO₄)

| Component | Sample containing 0.54% H ₂ O | Sample containing 0.63% H ₂ O | Sample containing 0.68% H ₂ O | Bulk composition |
|-----------------|--|--|--|-------------------|
| | grams/100 grams B | grams/100 grams B | grams/100 grams B | grams/100 grams B |
| PO ₄ | 12.9 | 15.0 | 18.1 | 18.6 |
| SO ₄ | 9.7 | 9.0 | 9.3 | 20.1 |
| NO ₃ | 48.0 | 46.9 | 43.4 | 28.9 |
| NH ₃ | 16.1 | 15.8 | 15.3 | 9.0 |
| K | 7.9 | 7.3 | 7.6 | 16.3 |
| Ca | 5.4 | 6.0 | 6.3 | 6.7 |

$$B = \sum (PO_4 + SO_4 + NO_3 + NH_3 + K + Ca) \text{grams}$$

Table 5 - SURFACE COMPOSITION OF NP 20-9

| Component | Sample containing 0.43% H ₂ O | Sample containing 0.66% H ₂ O | Bulk composition |
|-----------------|--|--|------------------|
| | grams/100 grams | grams/100 grams | grams/100 grams |
| PO ₄ | 24.4 | 25.0 | 33.8 |
| NO ₃ | 52.6 | 52.9 | 43.6 |
| NH ₃ | 19.7 | 17.9 | 14.4 |
| Ca | 3.3 | 4.2 | 8.2 |

c) Effect of temperature cycling on caking

NH_4NO_3 can exist as five different crystal modifications. Transition from modification III to modification IV is of particular interest in connection with the caking of NPK fertilisers. The transition from III to IV takes place at about 32°C . Modification IV (tetragonal) is stable from -18° to 32°C , while modification III (rhombic) is stable from 32° to 84°C .

The transition from IV to III is accompanied by a volume expansion of about 3.6%. The expansion is cumulative and irreversible.

In the case of NPK fertilisers produced by the Odda process and containing about 0.3% H_2O , there is a high probability of finding mostly modification IV after a few days storage at temperature below 32°C .

The effect of these crystal modification transitions on the tendency of NPK to caking has been investigated. 500 gram samples were temperature-cycled 2 to 4 times in the region of 22° to 40°C . The results are given in Table 6. The tendency to caking is increased as a result of the temperature cycling.

Table 6

| PRODUCT | % H_2O | CAKING NUMBER* AFTER n CYCLINGS BETWEEN 22° AND 40°C | | |
|-------------|------------------------|--|-------|-------|
| | | n = 0 | n = 2 | n = 4 |
| NPK 13-6-15 | 0.29 | 1580 | 1920 | 2060 |
| NPK 21-4-10 | 0.30 | 1400 | 2650 | 3880 |
| NPK 12-5-15 | 0.23 | 1650 | 1950 | 2100 |

* The caking number is a measure of the degree of caking. The test procedure has been evolved at Norsk Hydro Research Center.

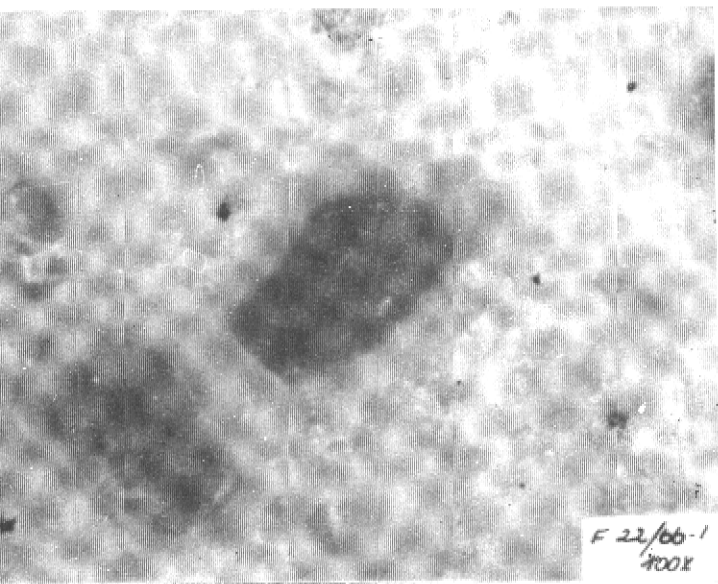


fig.1

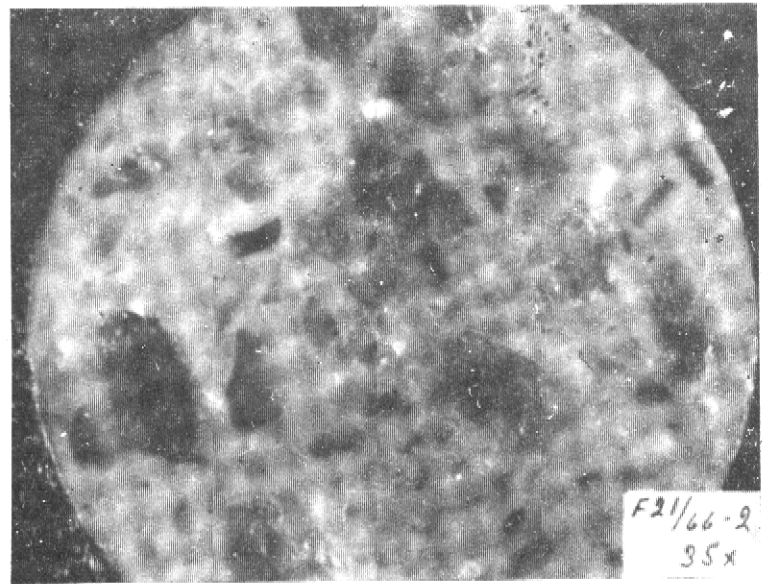


fig.2

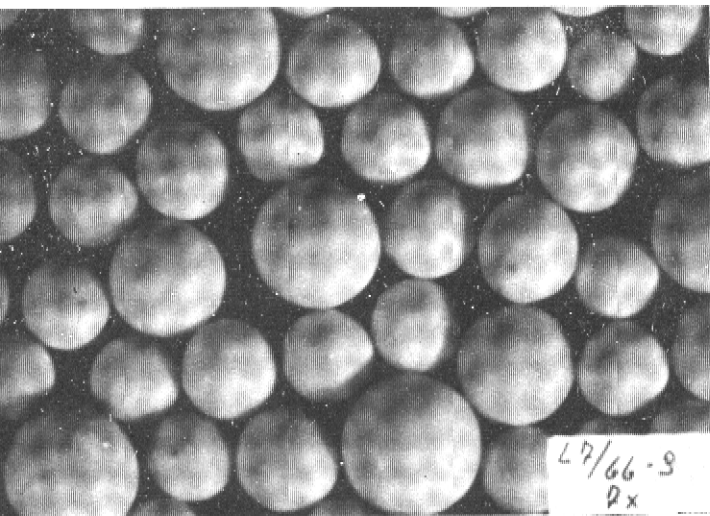


fig.3

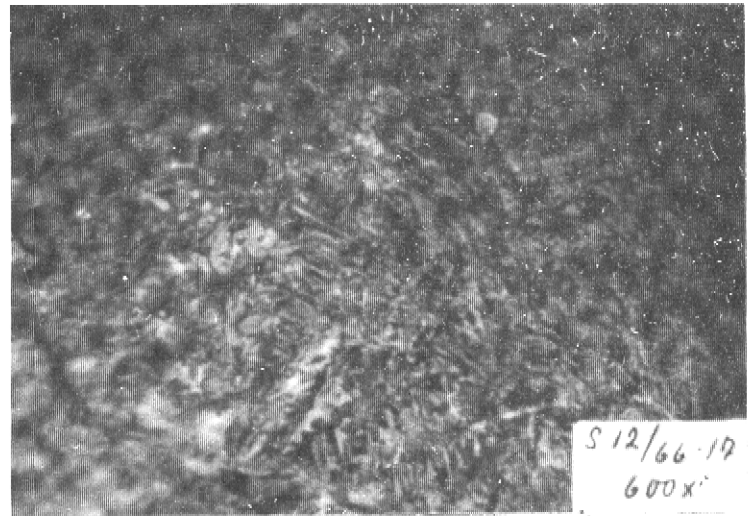


fig.4

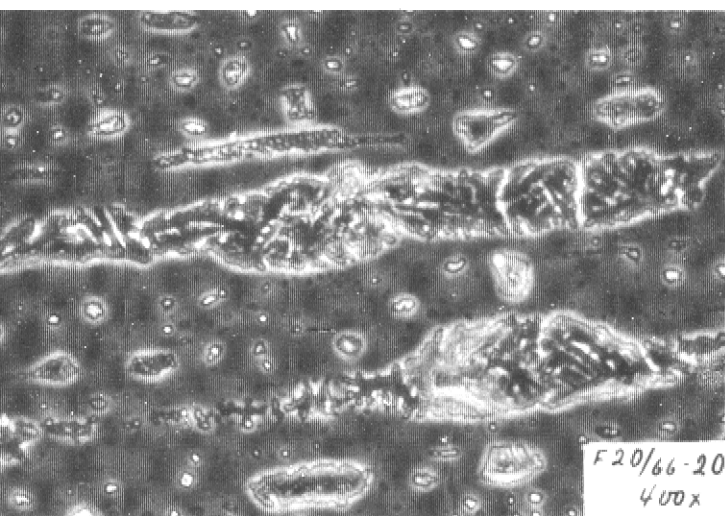


fig.5

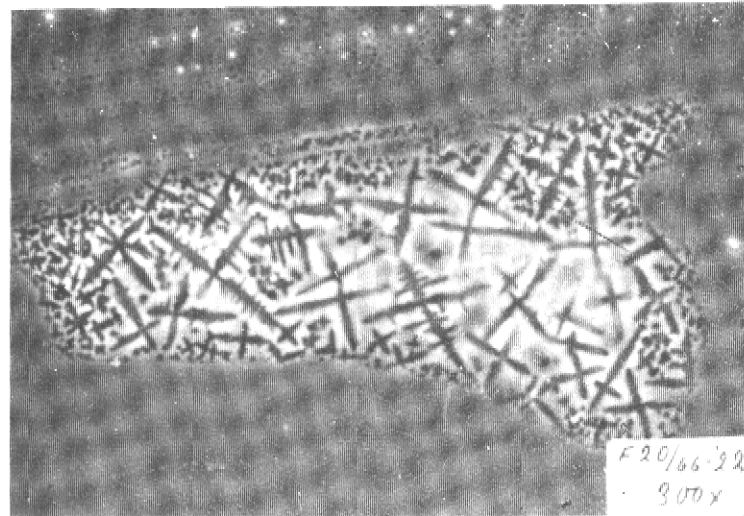


fig.6

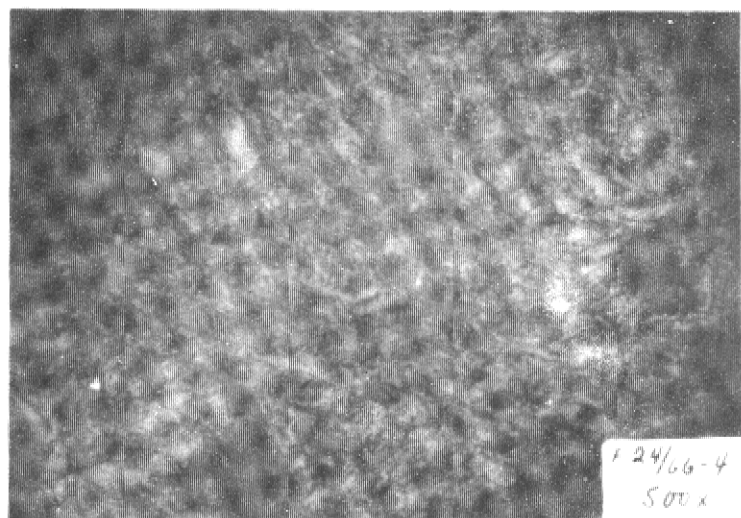


fig.7

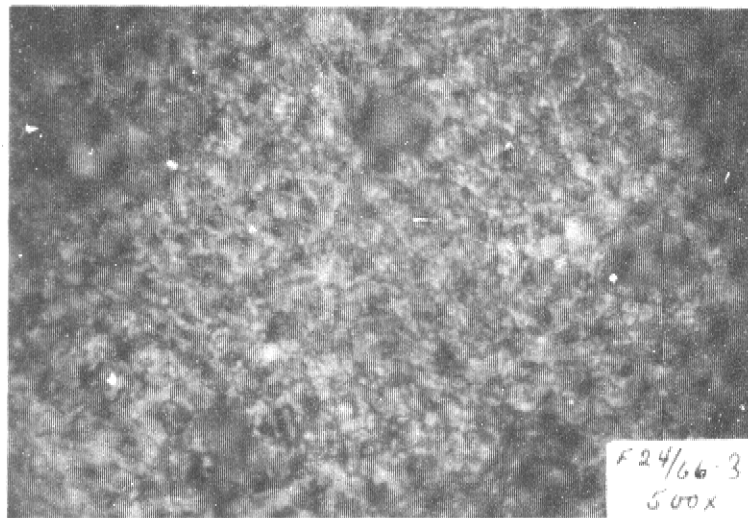


fig.8

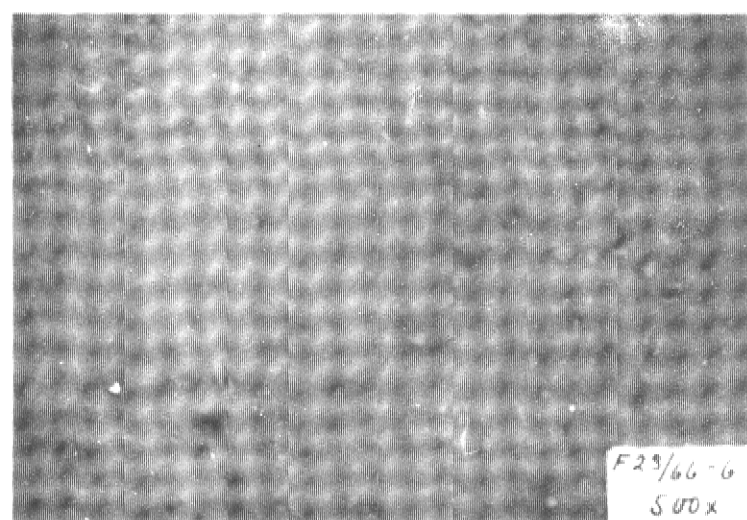


fig.9

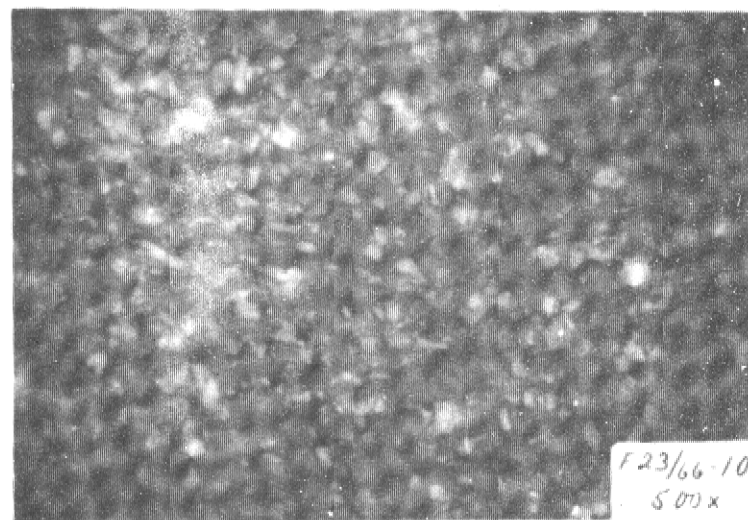


fig.10

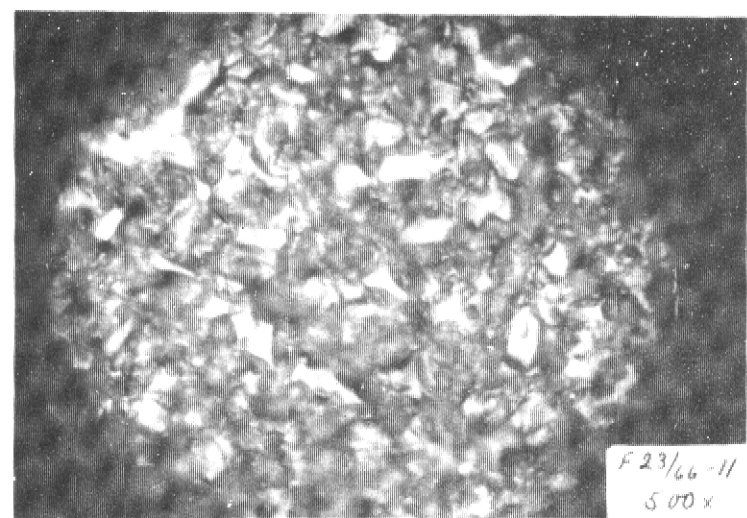


fig.11

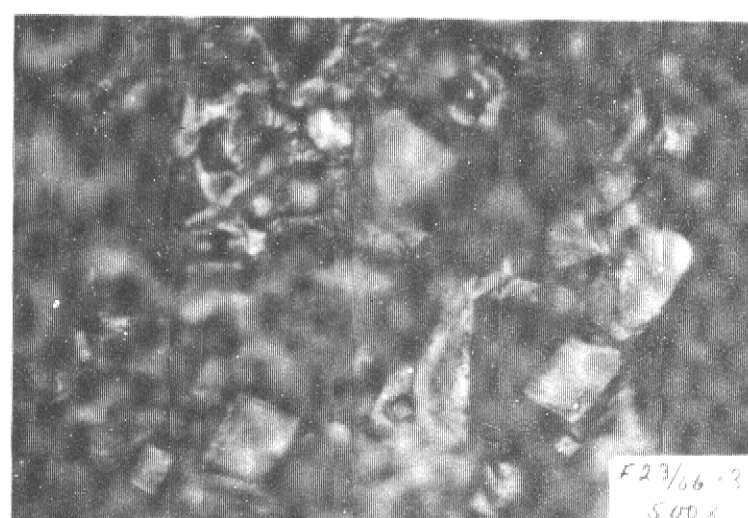


fig.12

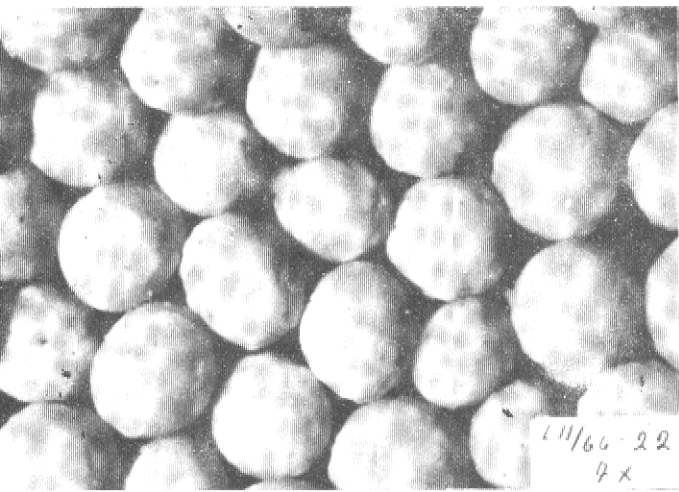


fig.13

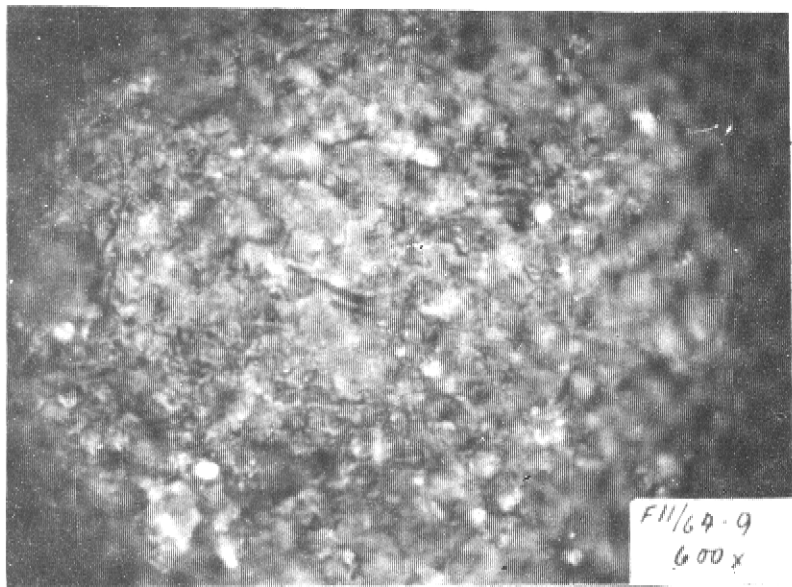


fig.14

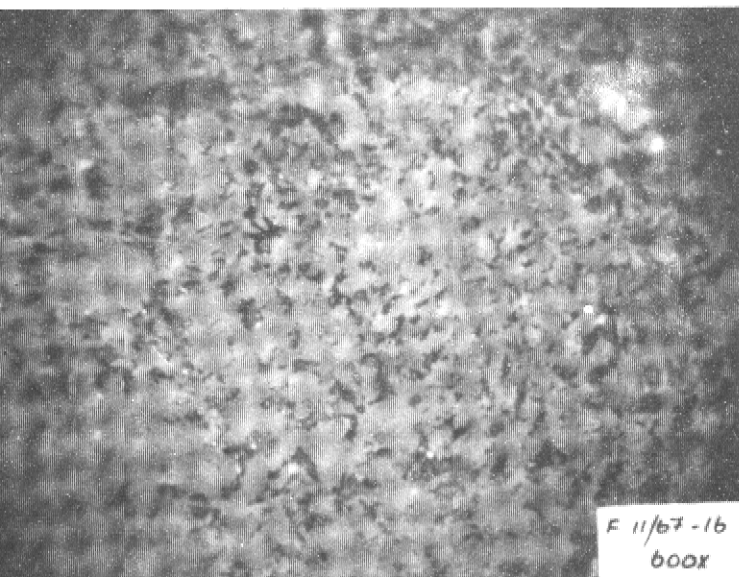


fig.15

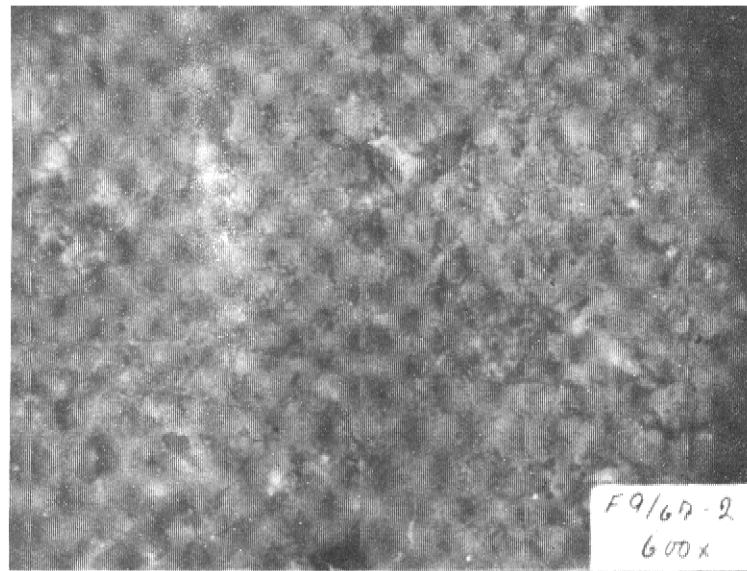


fig.16

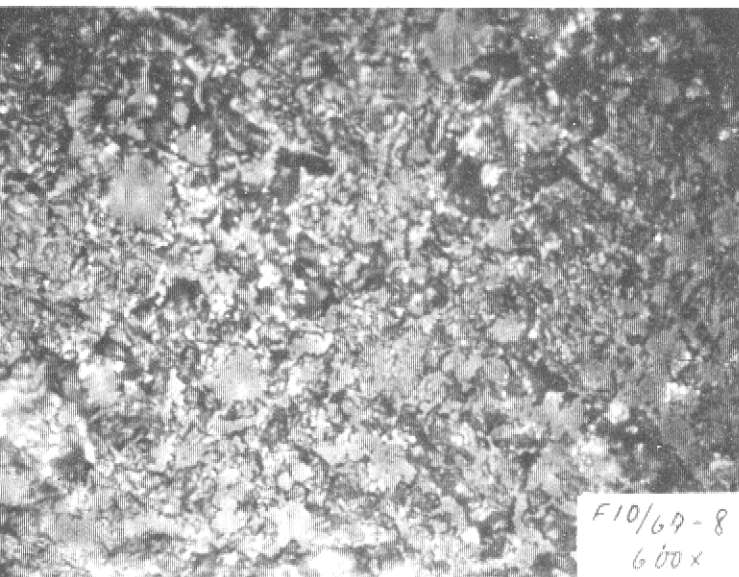


fig.17

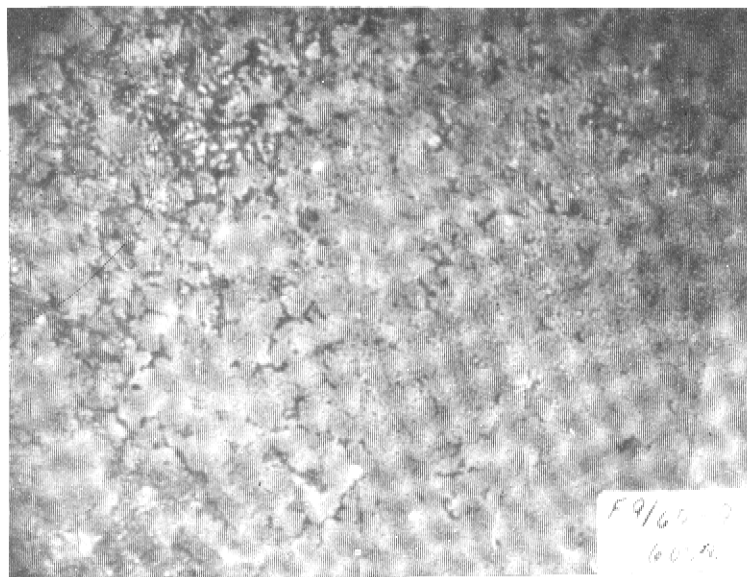


fig.18

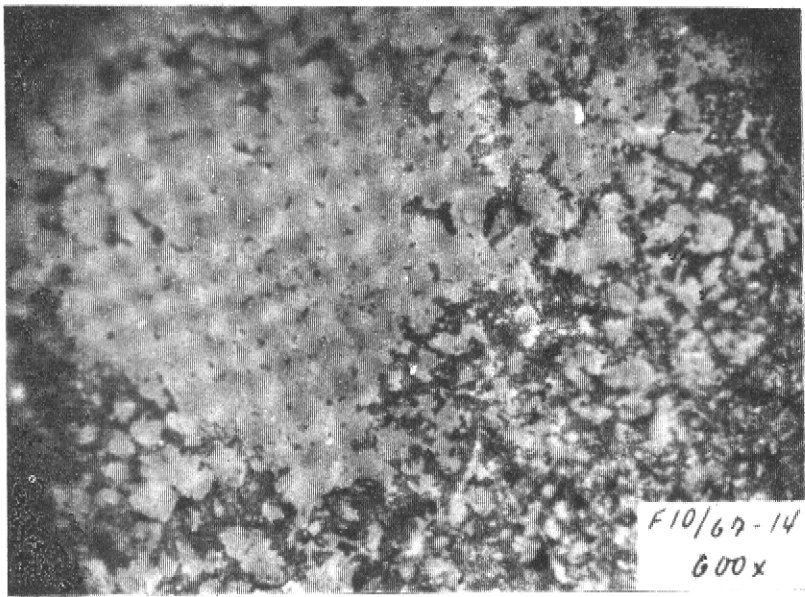


fig. 19

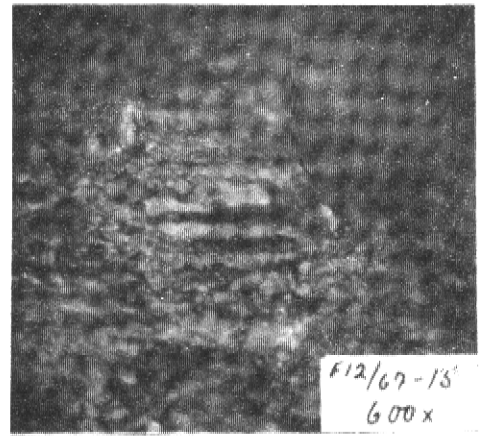


fig. 20

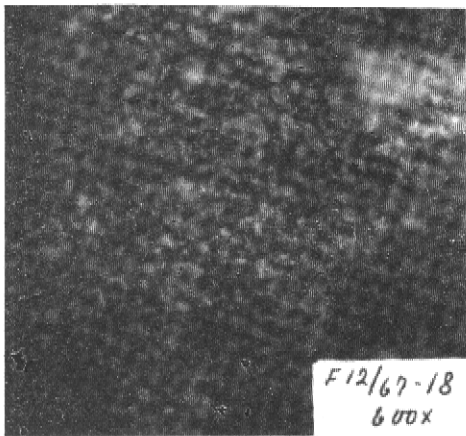


fig. 21

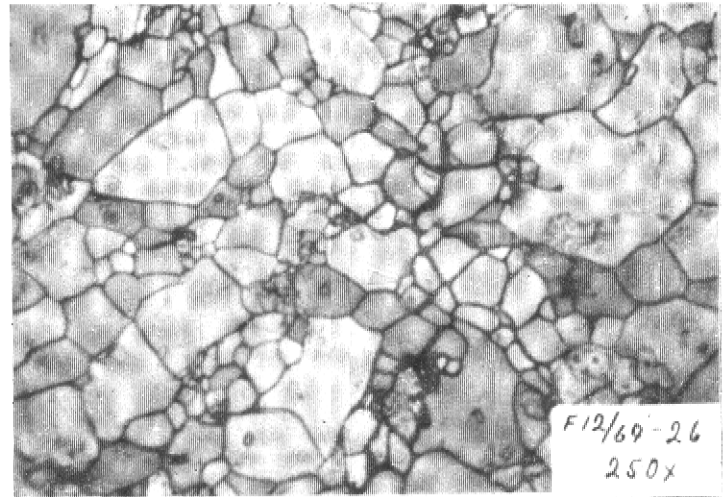


fig. 22

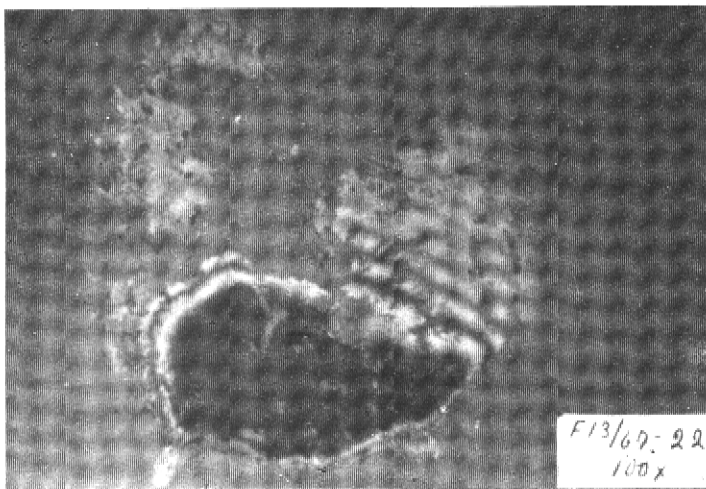


fig. 23

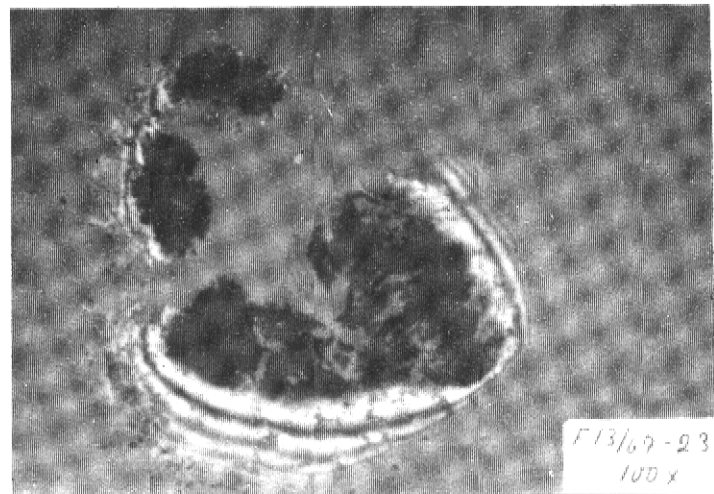


fig. 24

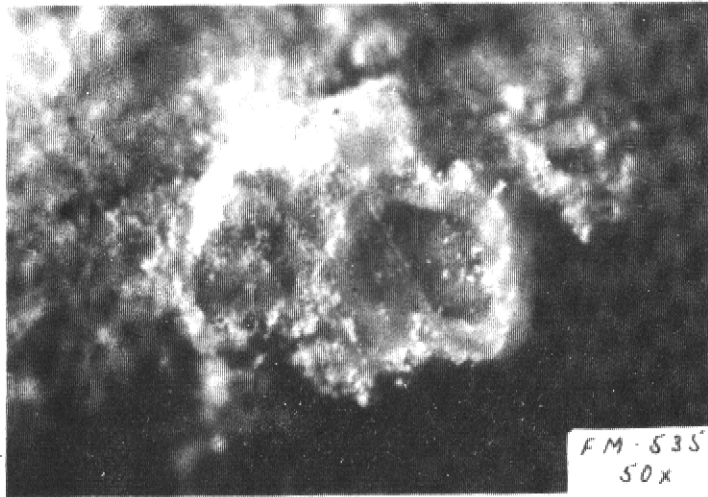


fig.25

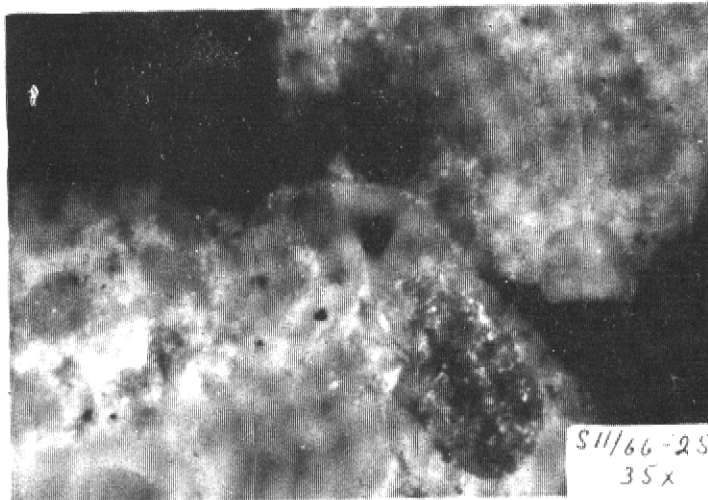


fig.26

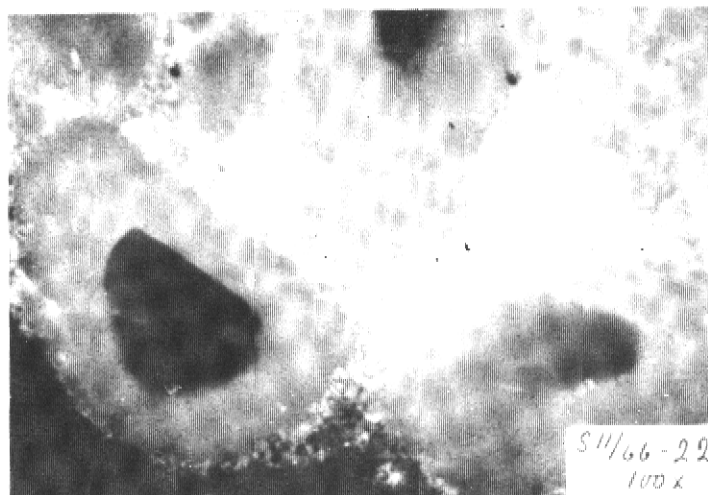
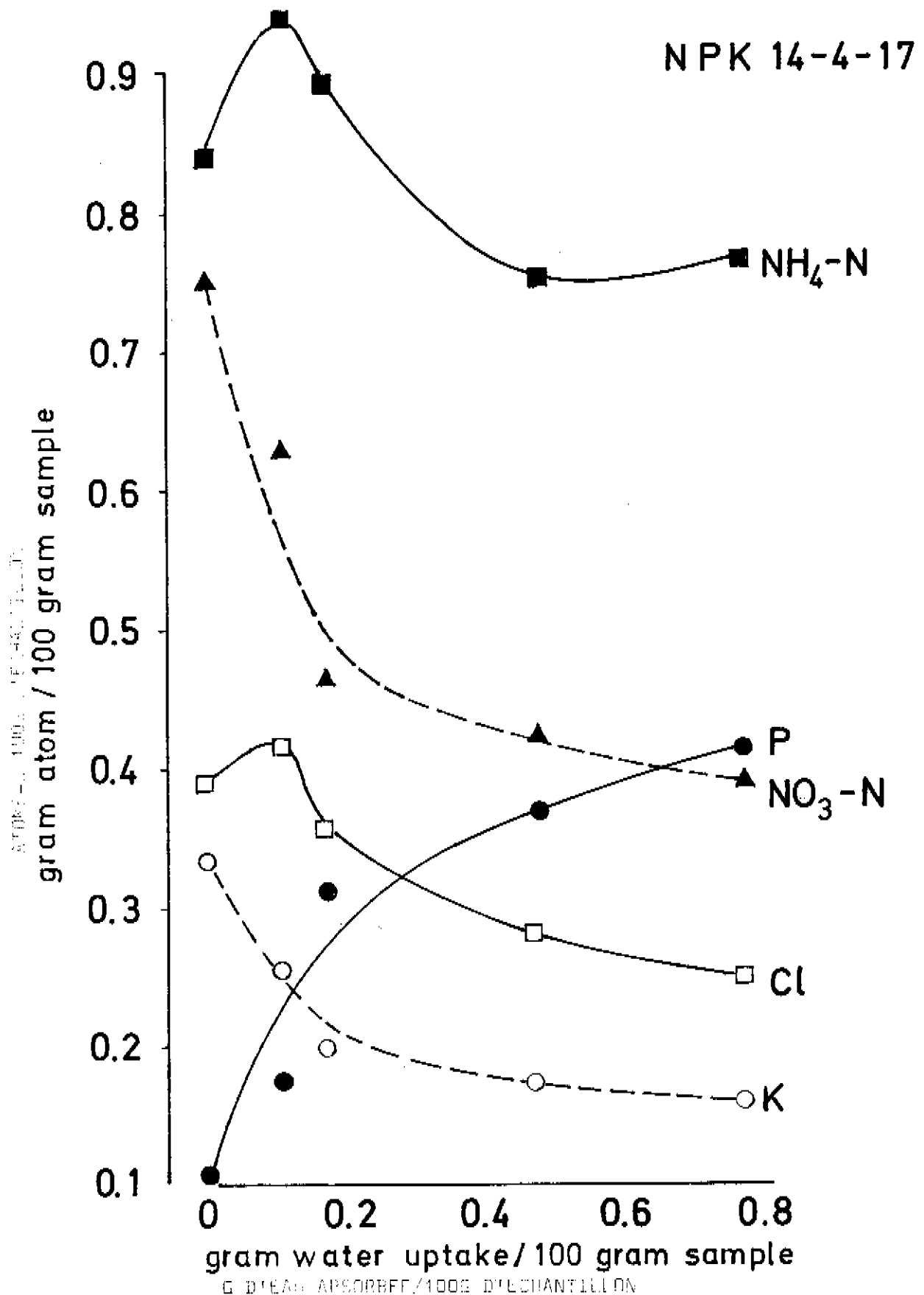


fig.27



Surface composition as function of water uptake

COMPOSITION DE LA SURFACE EN FONCTION DE L'EAU ABSORBÉE