## Title
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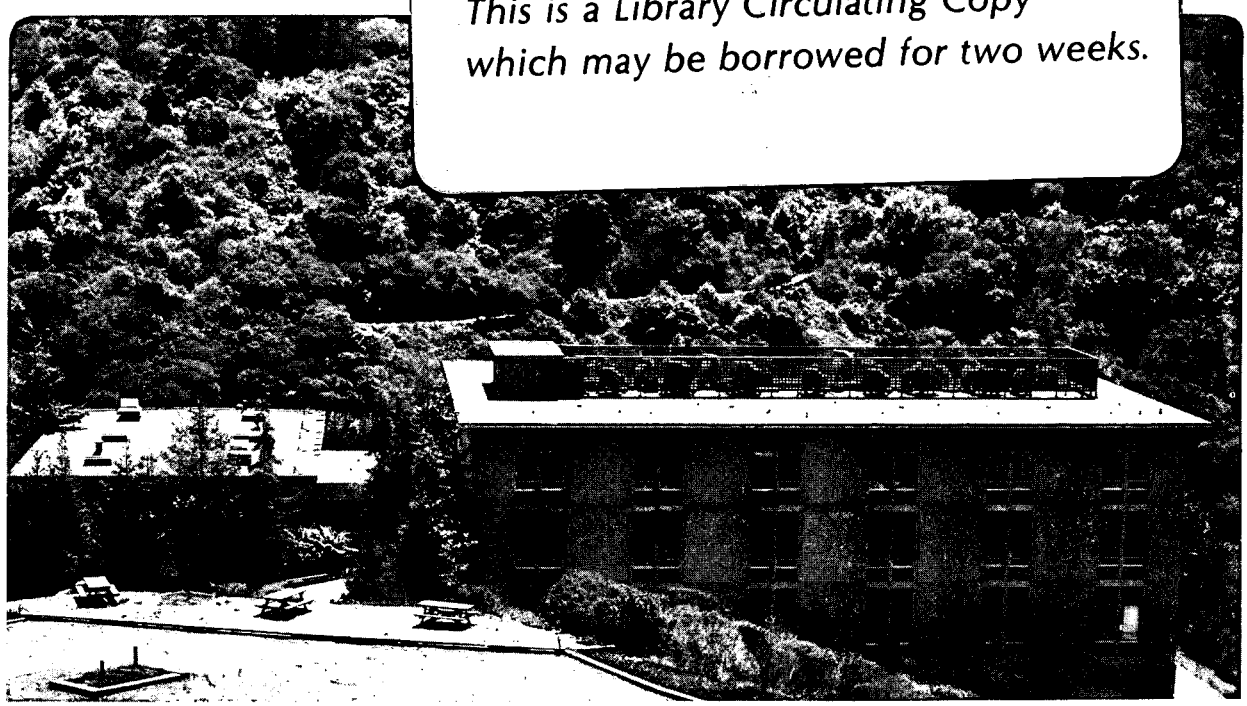

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# APPLICATION OF VIDEOMICROSCOPY TO *IN-SITU* STUDIES OF ELECTRODEPOSITION

by

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# APPLICATION OF VIDEOMICROSCOPY TO IN-SITU STUDIES OF ELECTRODEPOSITION

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## ABSTRACT

A videomicroscope has been set up for the continuous observation and recording of the developing surface morphology of electrodeposited metals in a channel flow cell. With a reciprocating, motor-driven traveling stage moving in the flow direction, quasi-simultaneous observation of several electrode areas is possible over extended periods of time. A dual eyepiece enables the experimenter to either observe the experiment in progress or to record still photos without destroying the video camera's alignment. With fiber-optic illumination, adequate light for good quality micrographs is provided. With a maximum magnification of 375X, an area of 300 $\mu$m x 200 $\mu$m can be observed at any one time with a diffraction limited resolution of 0.5 $\mu$m.

# INTRODUCTION

The evolution of surface morphology of electrodeposits is of considerable scientific and technological interest. Composition of the electrolyte, addition agents, current density, hydrodynamic flow, and the nature of the substrate play a significant role in the development of deposited metal layers. Many researchers have observed the surface structure ex-situ, i. e. following interruption of the deposition process. Ex-situ studies may be inadequate, because they don't allow the uninterrupted observation of the developing surface features over the long periods of time typically involved in the deposition of thick deposits. Preferentially, the growth of electrodeposits should be recorded in-situ, at a sufficient magnification to allow recording microscopic scale processes on the surface. In this report, a non-invasive technique is reported for use in the study of the surface features in the development of massive deposits.

Video microscopy is well known in the biological field; however, its use has not been reported for the study of electrodeposition processes(1). This method can be used to record the growth of micrometer-scale features over long periods of time, and the experimenter can review the progress of the developing surface morphology instantaneously. The videotape can be played over and over again, and measurements can later be taken from the recording. The tape can also be digitized by a computer for image enhancement and automatic analysis.

The addition of a videocamera provides another dimension to photography through the microscope. With electronic cameras, the progress of deposition can be observed instantaneously, and the microscope can be maneuvered so that a particular surface event is recorded. The images can be enhanced to reveal features that would otherwise be obscured by noise(1). However, care must be taken to ensure that artifacts are not introduced by the use of video. One of the most serious problems is lighting; if insufficient light, or improper lighting, is used, the resulting images are of poor quality. This problem is especially acute when using video cameras, because: (1) videotape has a lower resolution than photographic film; (2) video cameras are less efficient at gathering light; and (3) overly intense lighting can cause the sig-

nal to spill over into adjacent regions causing "hot spots" and "blooming", which lower contrast.

There are several differences between conventional photography and photography through the microscope, the most important being the role of the camera. In normal applications, the camera and the photographer compose the image and take the picture. The final form of the photograph is determined only by the camera settings. In contrast, the microscope is the primary factor determining the photographic composition in photomicrography(2); the camera acts mainly as a holder for the sensing medium. The front surface of the camera lens is placed at the eyepoint of the microscope, an arrangement minimizing vignetting. The camera is focused at infinity, and the camera's aperture is fully opened. Closing the camera's aperture does not improve the depth of field as it would in conventional photography, in fact, decreasing the size of the aperture opening only causes less light to strike the sensing medium, thus worsening the photomicrograph quality.

## EQUIPMENT AND FEATURES

The videomicroscopy system, assembled in our laboratory and pictured in Figure 1, is composed of several elements(3). At the far left is the video monitor and the video recorder which store and display the image of the developing deposit. The video camera is connected directly to the video recorder, an arrangement minimizing image degradation. As pictured in Figure 2, this device is mounted so that the microscope adapter (Sony MVA-11) takes the position of the human eye, and the entire arrangement is attached to a movable stage. Both the videomicroscope and the flow cell rest on an isolation stand.

To be useful in the study of developing morphological phenomena, the videomicroscopy system had to meet several basic requirements. Since the major events in the deposition process occur on the scale of several micrometers, the minimum system resolution had to be on

the order of 1 micrometer. However, because the deposition process was performed using a flow system and because the morphology is notoriously sensitive to the presence of impurities, the objective lens could not be placed in the electrolyte, as was done by a previous researcher (4). To accurately measure the sizes of protrusions with time, adequate sharpness and image quality were mandatory. Consequently, highly intense light and isolation from room vibrations had to be provided. To observe the same part of the electrode (chosen for reasons of current distribution), movement of the microscope stage in three dimensions was essential, because the electrodes were not identically positioned in their epoxy holders. Instantaneous review and still photography capabilities were also desired.

The flow cell used for this study, a schematic of which is pictured in Figure 3, had a channel depth of 3 mm. The flow cell was sealed using a 1 cm thick acrylic cover plate, and opposite the microscope objective, the acrylic plate was machined to accommodate a 2 mm thick glass window which is held in place by the cell cover. Because the clearance between the objective lens and the cell is substantially large, an objective lens with a working distance of at least 5 mm had to be used so that the objective lens can be placed outside the cell, a setup which is pictured in Figure 4. For normal lenses which provide resolution of the order of 1 $\mu$m, the working distance is only fractions of mm; therefore, objectives designed with a large working distance (retrofocusing lenses) were required. Such lenses provide working distances up to 10 times that of a normal objective with the same numerical aperture (magnification). The diffraction limited resolution is related to the numerical aperture (N. A. ) by the equation (5):

$$\text{Limit of resolution} = \frac{\lambda}{2\text{N.A.}}$$

where $\lambda$ is the wavelength of the light used. In the videomicroscope, a 50X Leitz/Wetzlar UMK lens with a N. A. = 0.6 and a working distance of 5.6 mm was used.

The videomicroscope system is currently capable of recording the progress of deposition at magnifications up to 375X, which allows observation of an electrode area of approximately 300 x 200 $\mu$m. With a more intense light source and a higher power eyepiece, a maximum magnification of 600X is possible. Using the 50X, N. A. = 0.6 long working distance objective lens, the diffraction limited resolution is 0.5 $\mu$m. However, the actual resolution is somewhat less because the 2 mm thick window introduces aberrations.

A major problem in microscopy is that the micrograph quality can be poor because of the lack of sufficient contrast in the image. If a more intense, fiber optic light source is used, the increased illumination causes the contrast to increase and the image quality improves. However, too much light can cause blooming and hot spots, a problem which is most severe in tube cameras but is not unknown in solid state cameras.

Likewise, micrograph quality can be affected by room vibrations which may not be evident. In our system, the vibrations are controlled in two ways: (1) the table upon which the microscope rests is cushioned using foam rubber, and (2) the microscope and flow cell are jointly mounted on a spring assembly. The combination of these two methods adequately dampen most environmental vibrations.

The anodes were placed in the sides of the flow channel so that the cathode could be observed, even though this meant that the current distribution over the cathode was less than perfectly uniform. An area where the current distribution was uniform was usually selected for photography. So that any area of the electrode surface could be examined, the microscope stage was designed for 3 dimensional movement. An automatic, reciprocating traveling stage, with a maximum traveling distance of 3 cm, was attached parallel to the x-axis, the flow direction, so that quasi-simultaneous observation of several areas of the electrode surface could be made. The scanning feature allows observation of extended electrode areas with high resolution, which is especially useful when studying flow phenomena, as one can record the effects of perturbations in the boundary layer upstream and downstream of protrusions.

One drawback of using conventional movie cameras to observe the progress of surface events is the delay involved in the processing of the film. This inconvenience is overcome by the use of videotape, although at a cost of resolution. In the videomicroscope system, the decrease in resolving power is minimized by the use of a high resolution, Sony 3/4 " U-matic video system (VO-5800H) which is shown in Figure 1. The larger format has a better resolution than the home format (340 lines distinguished in the middle of the screen vs. 260 lines) and is also more convenient for professional tape to film transfer.

The quality of photos taken with the video camera is strongly dependent on the mounting of the camera with the microscope. If the camera weighs more than a few ounces, properly orienting it at the eyepoint of the microscope will be difficult and aberrations will be introduced. As shown in Figure 2, a Javelin JE2062 camera, a compact, light-weight device specially made for microscopy, is employed in our setup. Because viewing capabilities for initial focusing were also desired, a dual eyepiece was installed and is featured in the schematic of Figure 4. A mirror was used to select an eyepiece; however, it may be possible to install a beam splitter that would allow simultaneous observation through both eyepieces.

To evaluate its capabilities, the video microscopy system described above was employed to observe the growth of zinc deposits from flowing, well supported, acidic chloride electrolytes. Synthetic graphite was the substrate for deposition. A range of cathodic current densities from 10-60 $mA/cm^2$ were used, and during the experiment, 400-500 $coulombs/cm^2$ were passed corresponding to a compact deposit thickness of 200 $\mu$m. Two distinguishable phenomena were observed: (1) the propagation of zinc striations, and (2) the presence of hydrogen bubbles.

Micrographs were made using a magnification of 160X, which corresponds to a video image width of 800 $\mu$m. Generally, the videotapes were recorded while the experiment was in progress and were then edited to produce time lapse movies showing the salient features of slowly occurring events. Still photographs were taken from the videotape with a Kodak

SV6500 color video printer.

In Figure 5, the development of striae from a set of unaligned protrusions is shown. As illustrated in Figure 5a, nodules initially are deposited randomly over the cathode surface. With the passage of time, the protrusions coalesce (as shown in Figure 5b), and some agglomerates become large enough to affect the flow in the boundary layer. The eddies formed reduce the mass transport overpotential causing the growth rate to increase in the direction parallel to the electrolyte flow, as shown in Figures 5c and d. As more charge is passed, the nodules coalesce to form ridges (Figure 5e), which then grow evenly in all directions.

In Figure 6, the growth of two large protrusions is tracked over 42 minutes. Over this time period, no new nuclei emerge in the spaces between nodules and only the largest protrusions grow significantly. As shown in Figure 6, the zinc crystals become elongated with the passage of more charge; this elongation occurs because of the changes in overpotential induced by the disruptions in the boundary layer flow.

The influence of bubble growth on zinc striation formation can also be examined with videomicroscopy. Figure 7 shows the growth of zinc in the presence of hydrogen gas evolution. Although there may be enhanced zinc deposition around a bubble (because of the current distribution), ridges are apparently not caused by hydrogen bubbles blocking the zinc surface; in fact, hydrogen bubbles appear to form preferentially on the peaks rather than in the valleys of ridges.

## SUMMARY AND CONCLUSIONS

For situations where microscopic processes are occurring, videomicroscopy can be used to observe and record the progress of deposition in real time. With long working distance lenses, the camera can be placed outside the electrochemical cell. The maximum

magnification in this type of system can approach 600X with a diffraction limited resolution 0.5 $\mu$m. Using a traveling stage, several areas of the surface can be quasi-simultaneously observed, which allows the experimenter to determine the consequences of surface events. When fiberoptic light sources are used, the images obtained can be of remarkably good quality.

## ACKNOWLEDGEMENT

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**Figure 1** Video microscope for studies of electrodeposition in a flow cell

A. Video screen showing image of developing deposit (the width of the image on the screen corresponds to 0.8 mm of the electrode surface); B. Electrical instrumentation; C. Video camera and microscope; D. Fiber optic illumination; E. Flow channel for deposition of zinc from acid chloride solution.

Inset shows electrode arrangement in the channel; Placement of anodes in the walls of the flow channel allows illumination and optical observation of the cathode surface.

Image on the video screen corresponds to the photograph depicting elongation of protrusions taken at 32 minutes following initiation of deposition, which is shown in Figure 6.

**Figure 2** Flow channel cell for zinc electrodeposition with videomicroscope and illumination device.

**Figure 3** Side view of flow cell used in videomicroscope studies.

A. Flow inlet; B. Flow outlet; C. Working electrode (0.5 X 1 cm); D. Auxiliary electrodes; E. Anodes (10 cm long); F. Optical glass window (2 cm diameter)

The cell dimension in the y- direction is 3 mm.

Note: The diagram is not to scale.

**Figure 4** Schematic of videomicroscopy system

A. Video camera; B. Microscope adapter lens; C. Eyepiece #1; D. Eyepiece #2; E. Objective lens; F. Mirror to switch between eyepieces; G. Cell window; H. Anodes; I. Cathode; J. Coarse focusing dial; K. Fine focusing dial; L. Automatic, reciprocating motor for travel-

ing stage; M. Z-stage; N. Spring table; O. Aluminum plate; P. Foam rubber; Q. Wood table; R. Optical glass window; S. Auxiliary cathodes.

The flow direction is perpendicular to the figure (x-direction).

Note: diagram is not to scale

**Figure 5** Genesis of a striation from a set of unaligned protrusions: (a) 1 min; (b) 3 min; (c) 5 min; (d) 10 min; (e) 20 min.

Deposition conditions: 3M $ZnCl_2$, 3M KCl, pH = 1.5, 28.5 mA/cm$^2$, Re = 4000, 800 $\mu$m/image.

The flow direction is from left to right.

**Figure 6** Elongation of protrusions with increasing time: (a) 10 min; (b) 15 min; (c) 21 min; (d) 32 min; (e) 42 min; (f) 52 min.

Deposition conditions: 1M $ZnCl_2$, 3M KCl, pH = 1, 18.6 mA/cm$^2$, Re = 1000, 800 $\mu$m/image.

The flow direction is from left to right.

**Figure 7** Effects of bubbles on zinc deposition during the growth of zinc ridges: (a) 18 min; (b) 30 min; (c) 40 min.

Deposition conditions: 1M $ZnCl_2$, 3M KCl, pH = 1.3, 55 mA/cm$^2$, Re = 1000, 800 $\mu$m/image.

The flow direction is from left to right.

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Fig. 1

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Fig. 2

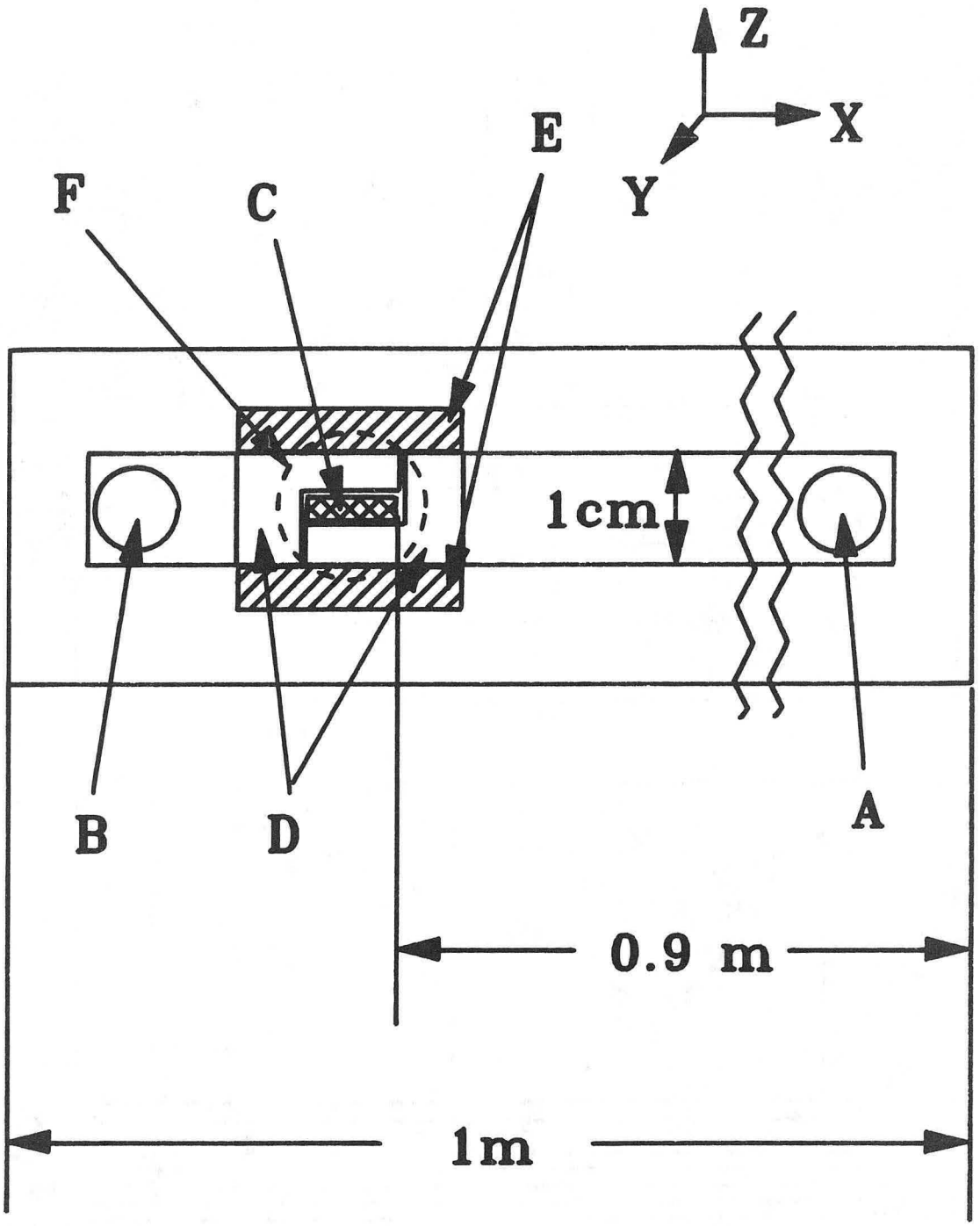


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Fig. 3

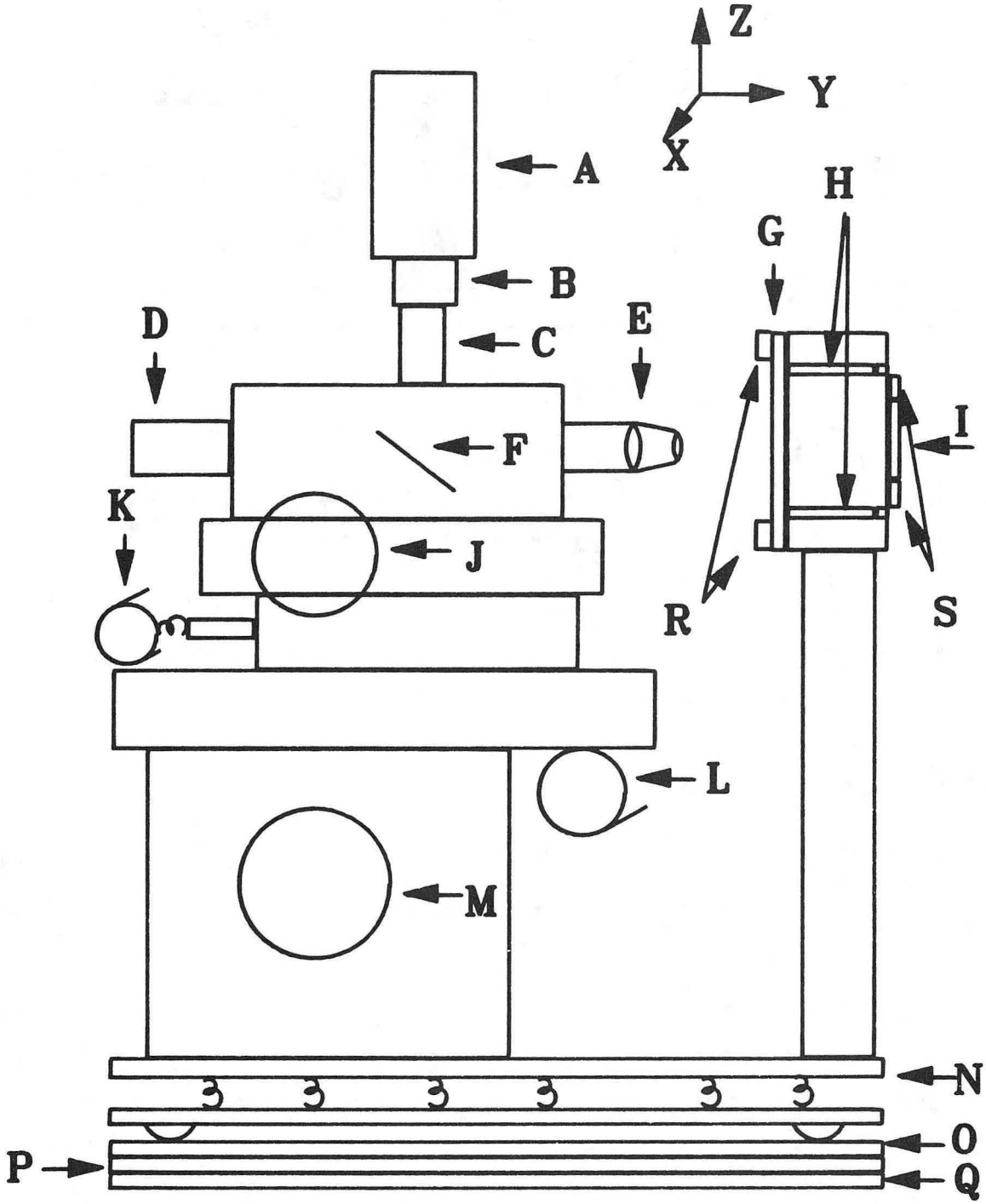


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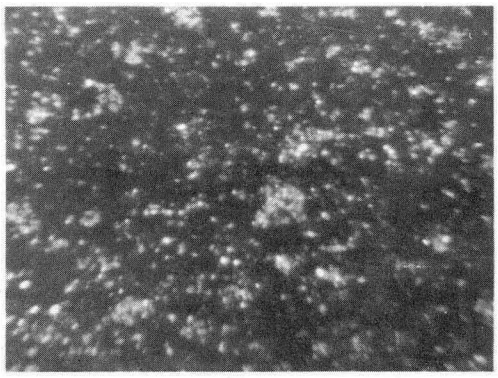
Fig. 4



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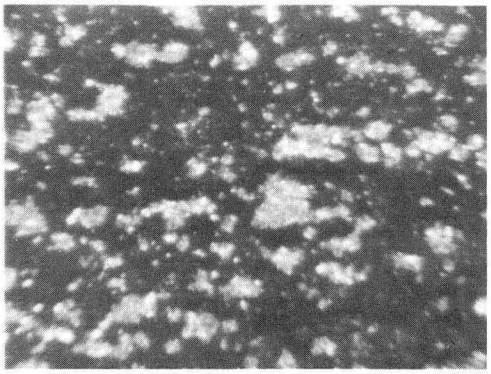

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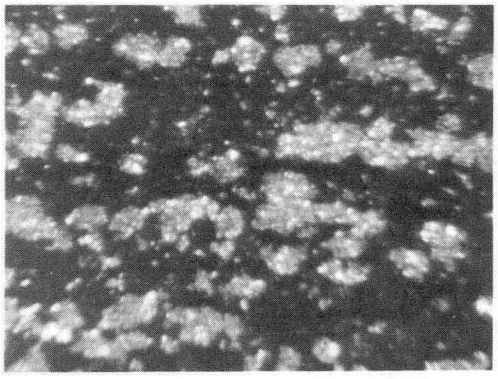

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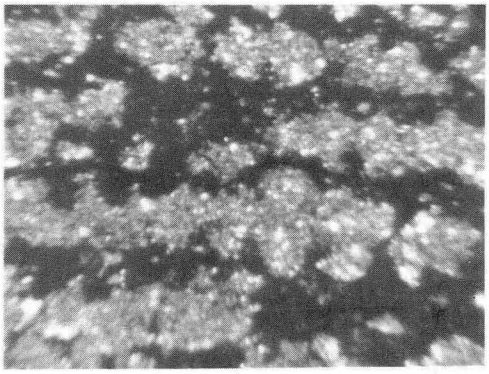

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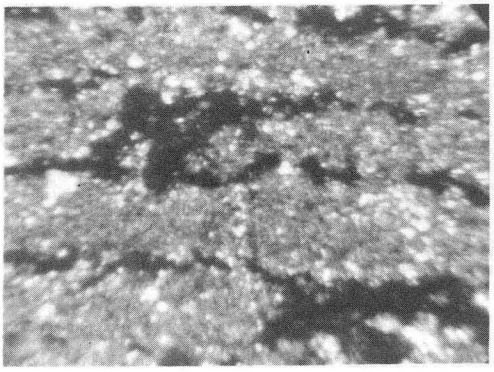

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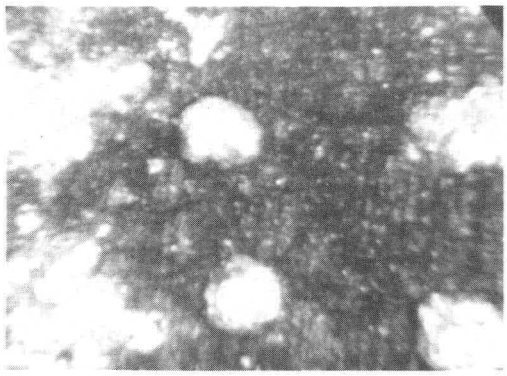
(e)

Fig. 5



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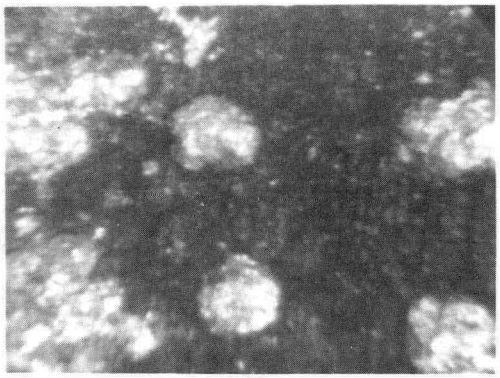

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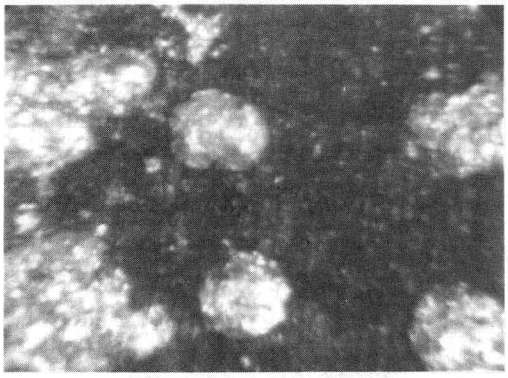

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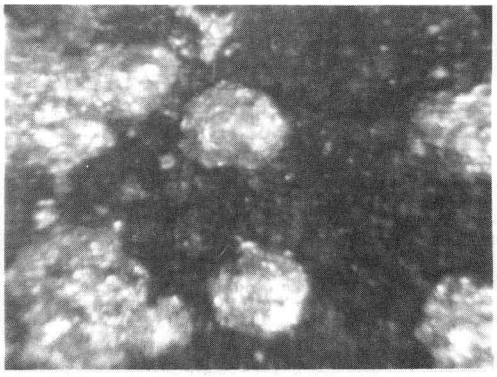

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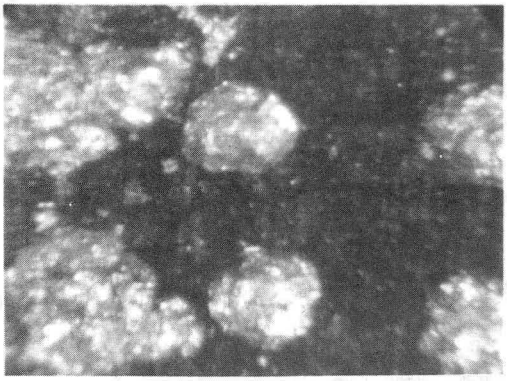

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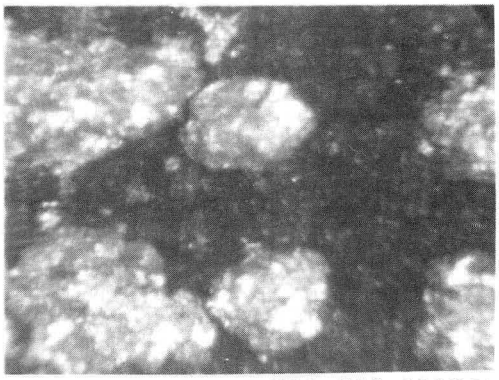

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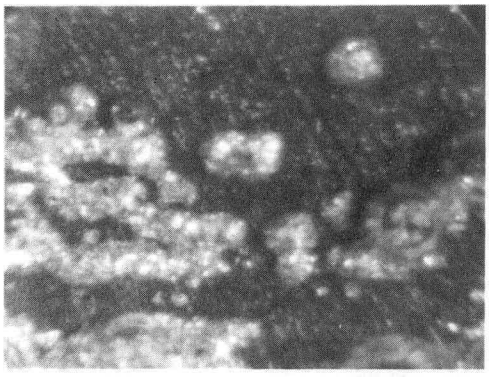
(f)

Fig. 6



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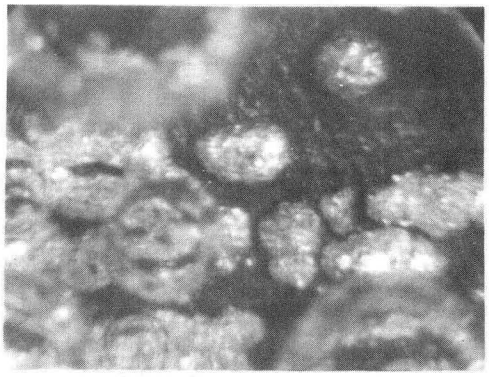

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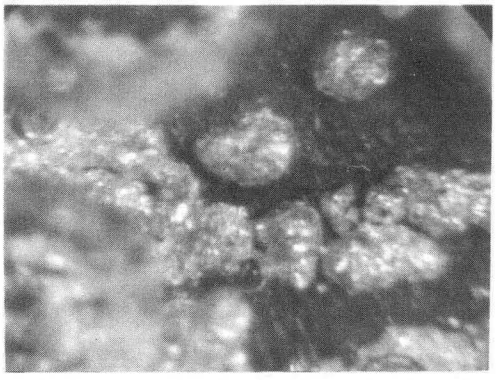

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(c)

Fig. 7

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