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THE CHEMICAL NATURE OF PAINT FILM SURFACES*

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In many ways, the most important part of a paint film is the surface of the film. The surface is also, possibly, the least known part of the film. Critical paint performance properties, such as adhesion, weatherability, and appearance, depend on the chemical nature of the surface of the paint film. Knowledge and control of the paint film surface, would seem to be an important step in controlling these important paint performance properties.

The only way one can determine the chemical composition of the surface of a paint film is by direct analysis. The surface of the film is different from the bulk of the film; it is not the same as the formula composition.

There are several reasons why this is so. First, surfaces, by their very nature, differ from bulk compositions. Second, surface activity phenomena - acting in the diverse mixture that is a paint - cause the surface to be different. Third, diffusion processes, oxygen and thermal gradients in drying paint films, insure that the surface layers of paints differ markedly from the bulk or formula composition.

This situation places importance upon the ability to determine the chemical composition of the surface of a paint film. In a fairly real sense, the surface of the paint film is the paint, and it is unknown.

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The Surface

The surface of a paint film may be defined as the upper 10 Å of film material. This is about a single molecular layer; this is the surface. Practically, the extent to which one approaches the analysis of the upper 10 Å of film surface is the extent to which one approaches surface analysis.

We developed a method for determining the chemical composition of paint film surfaces a few years ago in this laboratory. This method apparently allows us to approach rather closely, if not actually reach, true surface analysis. We estimate that we analyze about 25 - 50 Å of surface, and the qualitative nature of our results supports the idea that we are analyzing surfaces; the surfaces we determine are markedly different from the total film compositions.

The Method

We discovered that we could analyze the surface of a paint film by lightly polishing the surface of the film with potassium bromide powder, then collecting the powder - now contaminated with surface material - pressing it into a disc, and infrared analyzing the disc. This procedure yields an infrared spectrum of the film surface, giving the chemical composition of the film surface, as defined by the infrared spectrum.

This means that one can get a fairly comprehensive picture of the chemical nature of organic film surfaces because of the characteristic definition and broad applicability of infrared spectroscopy.

The problem, for this type of surface analysis, is to remove only a very thin layer of the surface, yet obtain a sample size that is satisfactory for infrared analysis.

To achieve this goal, we use a large film area, very light, uniform, abrasion, and efficient sample collection. We use 24" x 24" panels, giving an apparent film area of 3721.cm.^{2}. The film surface is lightly polished by rotating a fine steel wool pad amid potassium bromide powder scattered over the film surface. The potassium bromide plus sample is then collected with a vacuum device.

The surface abrasion apparatus is shown in Figure 1. The apparatus consists of two main parts: a panel support and carriage unit, in which the large sample panel rides, and a screw-drive traversing unit. The traversing unit carries the drive magnet back and forth across the panel.

The operation of the apparatus can be visualized with the aid of Figure 2. The abrading disc is composed of a bar magnet embedded in wax in an aluminum cup. This cup fits into an outer cup to which a steel wool pad is wired. This abrading disc is caused to rotate and traverse the panel by the action of the drive magnet, as seen in Figure 2. The white lines on the dark paint surface are patterns of swirled potassium bromide powder, caused by the rotation and traverse of the abrasion disc.

The abrasion discs are shown in Figure 3. The lighter discs are used for softer films, the heavier discs for harder films. The discs rotate at 300 rpm and traverse the panel at 2 ft. per minute.

The panel is moved 3-inches manually at the end of each traverse so that with these two motions the whole panel surface is abraded uniformly and reproducibly.

The steel wool used for the grinding disc is solvent washed and dried before use. Depending upon the hardness of the surface being analyzed, we used #0000, #00, or #0 steel wool. For the very lightest possible abrasion we do not use any steel wool; the potassium bromide powder (1.5 grams) is sprinkled evenly over the film surface and then simply collected with the vacuum collector. Surface sample is obtained in this way.

After surface abrasion, usually one or two times over the film surface, the potassium bromide powder, plus the surface sample, is collected by sweeping over the film surface with the vacuum-cyclone separator collector. This collector is shown in Figure 4.

To operate the collector, a vacuum line is attached at the top of the collector. As the vacuum foot is drawn over the film surface, the sample is aspirated into the collector and deposited in the sample cup at the bottom of the cyclone separator. With this procedure about 95% of the potassium bromide powder used is recovered.

The collected sample is 200-mesh screened, small steel wool fibers are removed with a magnet, and the powder is pressed into a transparent 13 mm. disc in a potassium bromide die in the conventional manner[1].

The infrared spectra were obtained with a Perkin-Elmer Model 21 double beam spectrophotometer, using a blank KBr disc in the reference beam. An ordinate scale-expander attachment for the spectrophotometer allowed increases in detection sensitivity of up to 75 times. This allowed us to analyze very small (thin) surface samples.

Bulk or total film samples (about 1.0 mg.) were ground with KBr powder in a mechanical vibrator, then pressed into discs for infrared analysis. This gave us the total film spectrum of the film.

Water Absorption by Potassium Bromide

There is no problem due to the absorption of water vapor by the potassium bromide powder during the abrasion process under normal laboratory conditions. The reason may be that there is very little grinding of the potassium bromide; no significant reduction in particle size, in the abrasion process. The abrasion time is short, usually less than five minutes; so that the potassium bromide is not long exposed to atmospheric water vapor.

In contrast, grinding potassium bromide in a mechanical vibrator gives strong water absorption bands in the spectra. Compensation, using similarly prepared control discs, is the only way to minimize this effect.

Estimation of the Thickness of Surface Removed in Abrasion

An important question about the method concerns the extent to which the goal of true surface analysis is achieved, the analysis of only the top 10 Å of film surface. This requirement is qualified, however, by the possibility that actual surface compositions are more than a single molecular layer thick. Surface compositions, as thick as 5 - 10 molecular layers, would mean that one could remove 50 - 100 Å of surface, and still determine the true surface.

Qualitatively, our results suggest that only very thin surface layers are removed in our surface abrasion. The surface compositions found are quite different from the total film compositions, and are not detected in total film infrared analysis. Further, successive surface analyses show nearly the same surface compositions, indicating relatively thick surface layers and/or very thin surface layer removal. In our lightest abrasions, there is no visual evidence of abrasion, even after several successive surface analyses.

We have made a rough quantitative estimate of the thickness of surface layer removed in abrasion. Using the film area of 3721. $cm.^2$, an approximate film density of 1.0 gm/cc., and a surface sample weight of 0.2 mg. (estimated from the intensity of the spectrum), we obtain an average film thickness equivalent of sample of

$$\frac{0.0002 \text{ gm.}}{1.0 \text{ gm/cc.} \times 3721. \text{ cm.}^2} \approx 5.4 \text{ Å}$$

This estimate is only approximate for several reasons, but even if it is in error by a factor of 5, it still suggests that we are only removing about 25 Å of surface.

We plan to attempt a direct measurement of the amount of surface removed at a later date.

Results of Some Surface Studies

Four examples of simple applications of film surface analysis are given in the following sections.

1. The Surface of a Paint Containing Silicone Oil

An appropriate initial test of a paint film surface analysis method is the detection of a surface active agent at the surface of a paint film. A successful result amounts to a rough certification of the method.

We analyzed the surface of a finish containing 200 ppm. silicone oil. Our results are shown in Figure 5. The spectrum of the film surface is that of silicone oil; it is completely different from the spectrum of the total film. The spectrum of the total film shows no trace of silicone oil. The method has passed a first rough test of validity.

2. Pigment and Silicone Distribution at a Paint Film Surface

It is reasonable to expect that if one could measure the distribution of a surface active material in a film near the surface, one would find a high surface concentration that decreased rapidly a short distance into the interior of the film. On the other hand,

the distribution of pigment near the film surface might be expected to be just the reverse. Paint chemists have long speculated that pigmented paint films have a clear film layer at the film surface - free of pigment. Our studies on a pigmented finish, containing 500 ppm. silicone oil at a pigment/binder weight ratio of 50/100, provide data on these questions.

We made several successive surface analyses on the surface of this finish, and our results may be seen in Figure 6.

Both distributions are as expected. The silicone concentration is very high at the surface and decreases sharply a short distance into the film. This appears to be the expected behavior for a surface active agent in a film and this suggests that our method of measuring the silicone concentration - as the silicone ratio - is probably valid. The silicone ratio is the ratio of the absorbance of a silicone band (12.5 microns) to a film band (5.8 microns).

The pigment distribution curve suggests there actually is a layer of clear film (binder) over the pigment at the paint film surface. The measured pigment concentration is zero at the surface and increases gradually going toward the interior of the film. We measured the pigment concentration as the ratio of pigment to binder using the absorbance of the 14.5 micron pigment band and the absorbance of the 5.8 micron binder band.

Note that the surface levels of both are quite different from the total film levels as shown at the lower right of the Figure. As measured in the total film, the silicone ratio is zero and the pigment absorbance ratio is nearly one.

The units of film thickness shown in the graph are the sample absorbances at 5.8 microns; they are proportional to film thickness. A rough estimate suggests that the total film thickness removed in this study may have been about 0.01 mil.

The pigment distribution results raise the question of how small pigment particles are in a paint film. If we remove a film layer estimated as 25 - 50 Å thick, are there pigment particles this small in the paint film?

It is possible that there may be, and that the smallest particles might concentrate nearest the film surface. This size (50 Å) is below the level classified in pigment particle size distribution measurements; where as much as 10-20% (by weight) of the pigment particles may be classed as below 0.1 micron (1000.Å).

Our present belief is that there may be pigment particles this size, and that the distribution curve shown may be valid. The alternatives are that the abrasion shears off portions of pigment particles or removes large pigment particles from the film. We do not presently believe either to be probable.

3. The Surface of a Polyethylene Film

As a second test of the general performance of this method of surface analysis, we analyzed the surface of a film of commercial polyethylene. We found, again, that the surface is quite different from the total film composition. The surface layer is a long chain amide. This amide is probably a slip-agent; similar materials are frequently added to polyethylene at a few hundred parts per million to improve film slip. The surface and total film spectra are shown in Figure 7.

This result also suggests that we are doing actual surface analysis and shows that free polymer films may be surface analyzed in this manner.

4. The Concentration of Plasticizer at a Paint Film Surface

Surface studies on a lacquer type paint film revealed that the phthalate plasticizer concentrated at the film surface. The formula ratio of plasticizer/polymer for this lacquer was 4/10; surface analysis revealed that the surface plasticizer ratio was about 8/10.

We then measured the surface plasticizer level as a function of the plasticizer level in the total film. The results are shown in Figure 8. The graph shows that only at the 2/10 plasticizer level is the surface level the same as the total film level. Above this film level, the surface plasticizer level rises rapidly, reaching a maximum

at 20/10 plasticizer ratio, for a film level of 7/10. Above this level, apparently the plasticizer compatibility with the film increases, causing a decrease in the surface concentration.

Surface Modification by Abrasion

A serious objection to this method would exist if the surface abrasion chemically changed a significant fraction of the surface sample. Our results have not shown indications of such changes.

The first evidence that this abrasion does not alter the surface sample is that, in the analysis of films drying by solvent evaporation, where there is the least opportunity for surface chemical change during film formation, the surface spectra we find are those of a film component, such as a plasticizer, unmodified. There is no evidence of chemical change.

The second evidence is that the surface analysis of polyethylene films, carried out in both oxidizing and inert atmospheres, has given the same results. The surface spectra were identical, when the analyses were done in oxygen and nitrogen atmospheres. It is reasonable to expect that these different conditions would magnify differences caused by the abrasion of the film surface, if such differences existed.

The question of surface sample modification by the abrasion process is still, however, a continuing question.

Summary

We have briefly described a method for determining the chemical nature of the surfaces of paint films based on the light abrasion of the film surface with potassium bromide powder, followed by palleting this powder, and infrared analysis. The method appears to be relatively simple and reasonably sensitive.

Using this method we have determined the chemical compositions of some paint film surfaces. The method also appears to be of possible utility for the cross-sectional analysis of paint films.

Because many important performance properties of paints, such as adhesion and durability, are surface properties - the ability to analyze paint film surfaces should be of considerable value in understanding the behavior of paints.

Acknowledgement

I would like to acknowledge the capable assistance of Edward J. Reilly in this work. I would also like to thank the du Pont Company for permission to publish this material.

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(1) Scheidt and Reinwein, Z. Naturforschung 76, 270-77 (1952)

Stimpson and O'Donnell, JACS 74, 1805 (1952).

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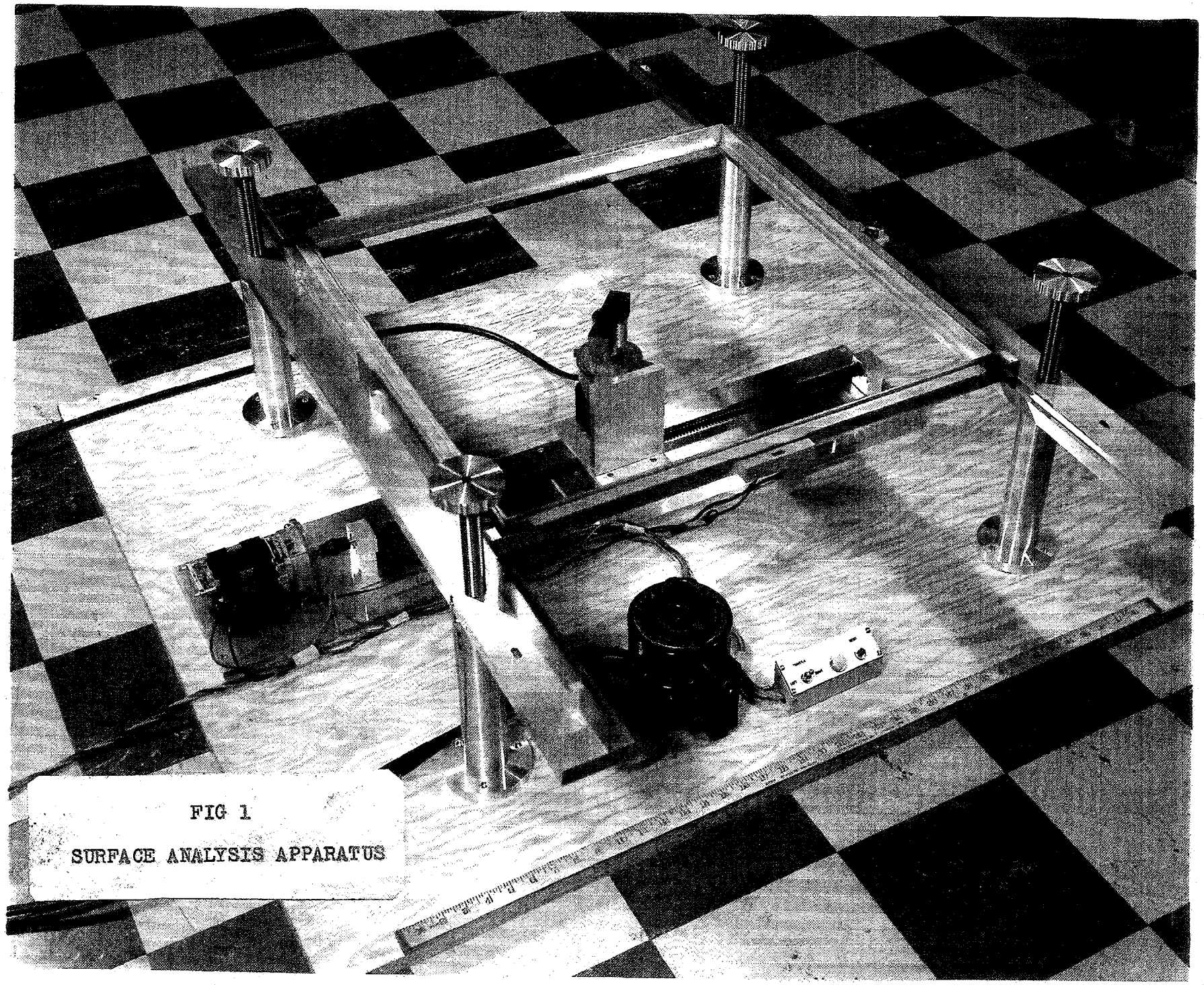


FIG 1

SURFACE ANALYSIS APPARATUS

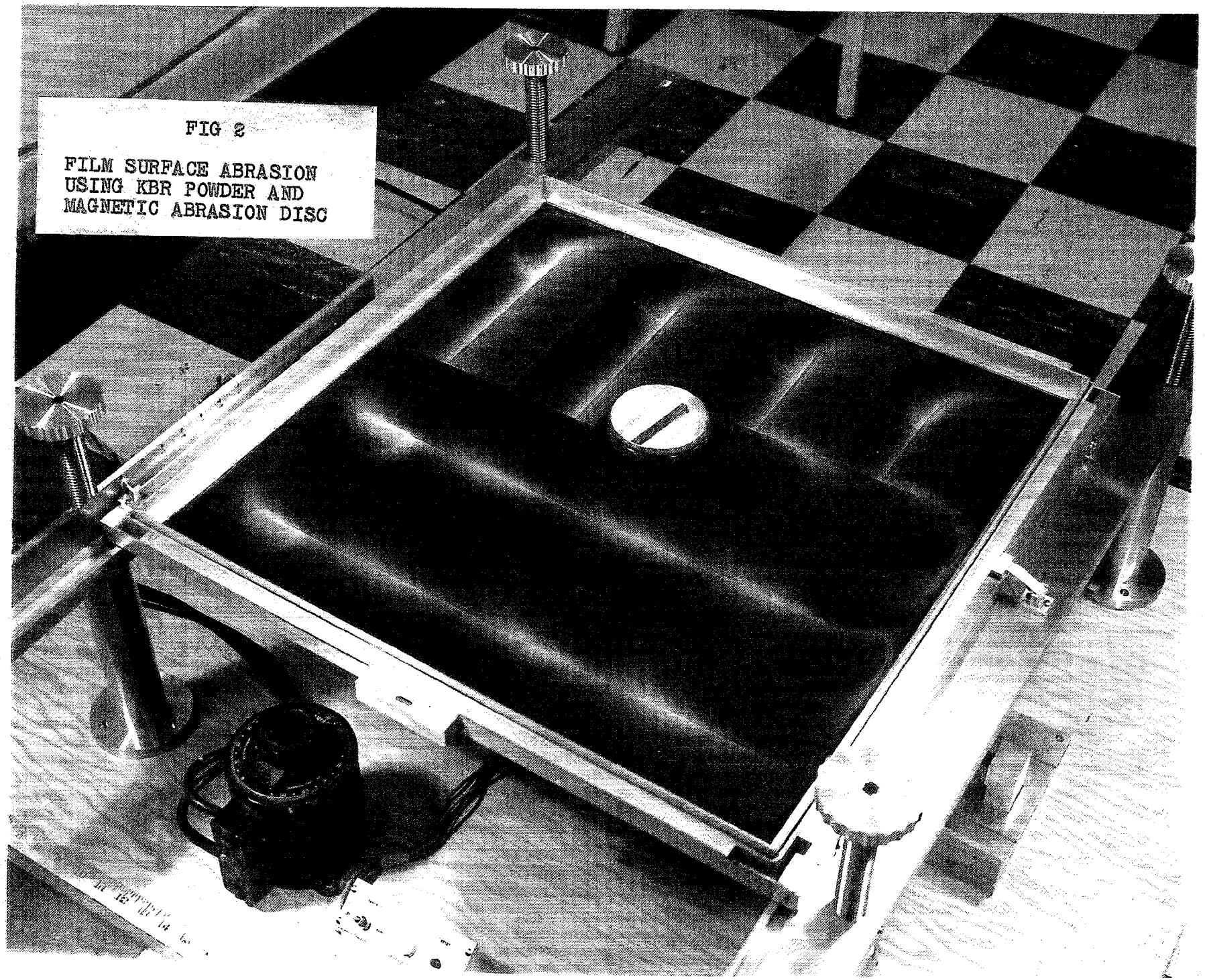
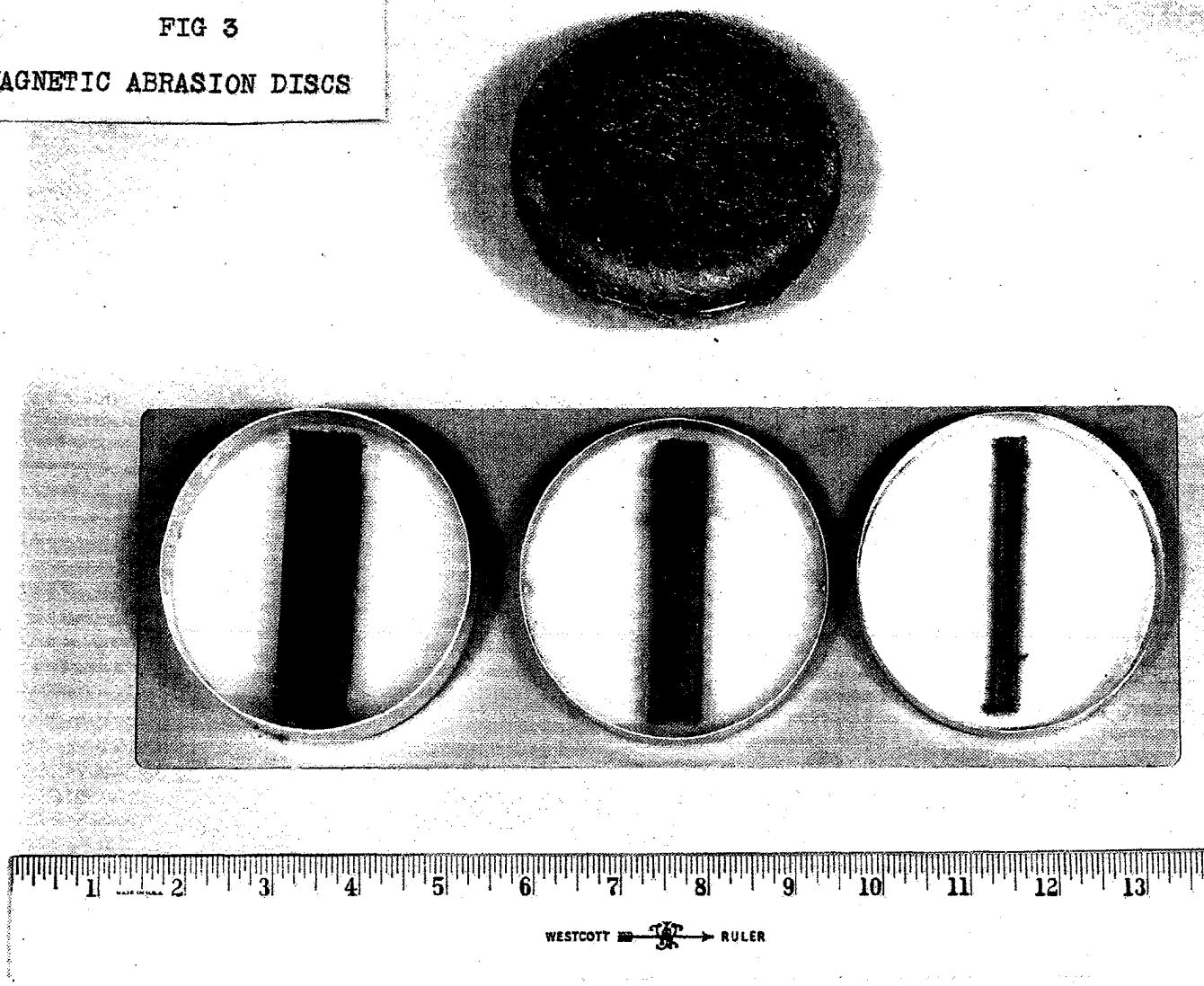


FIG 2

FILM SURFACE ABRASION
USING KBR POWDER AND
MAGNETIC ABRASION DISC

FIG 3

MAGNETIC ABRASION DISCS



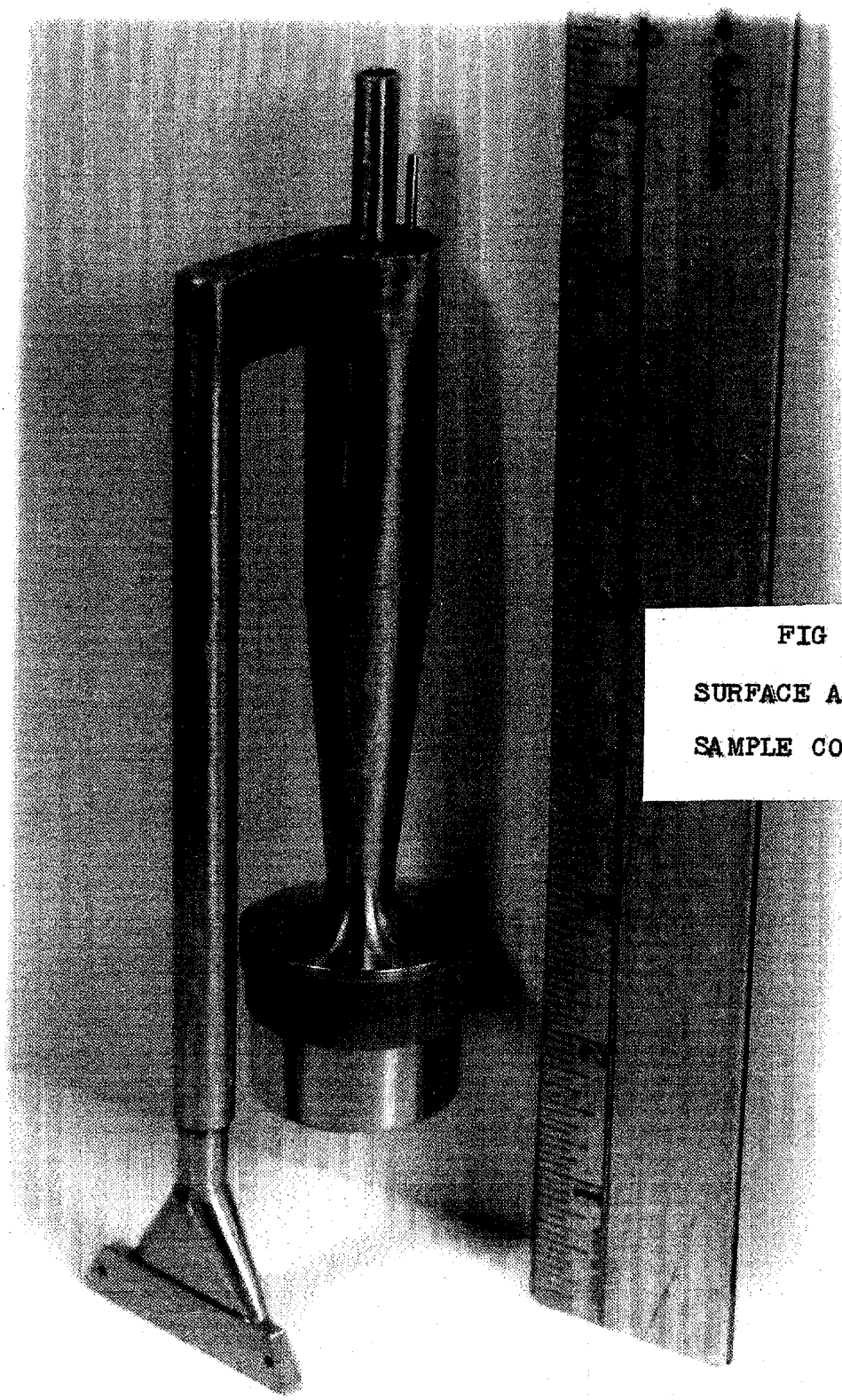


FIG 4

SURFACE ANALYSIS

SAMPLE COLLECTOR

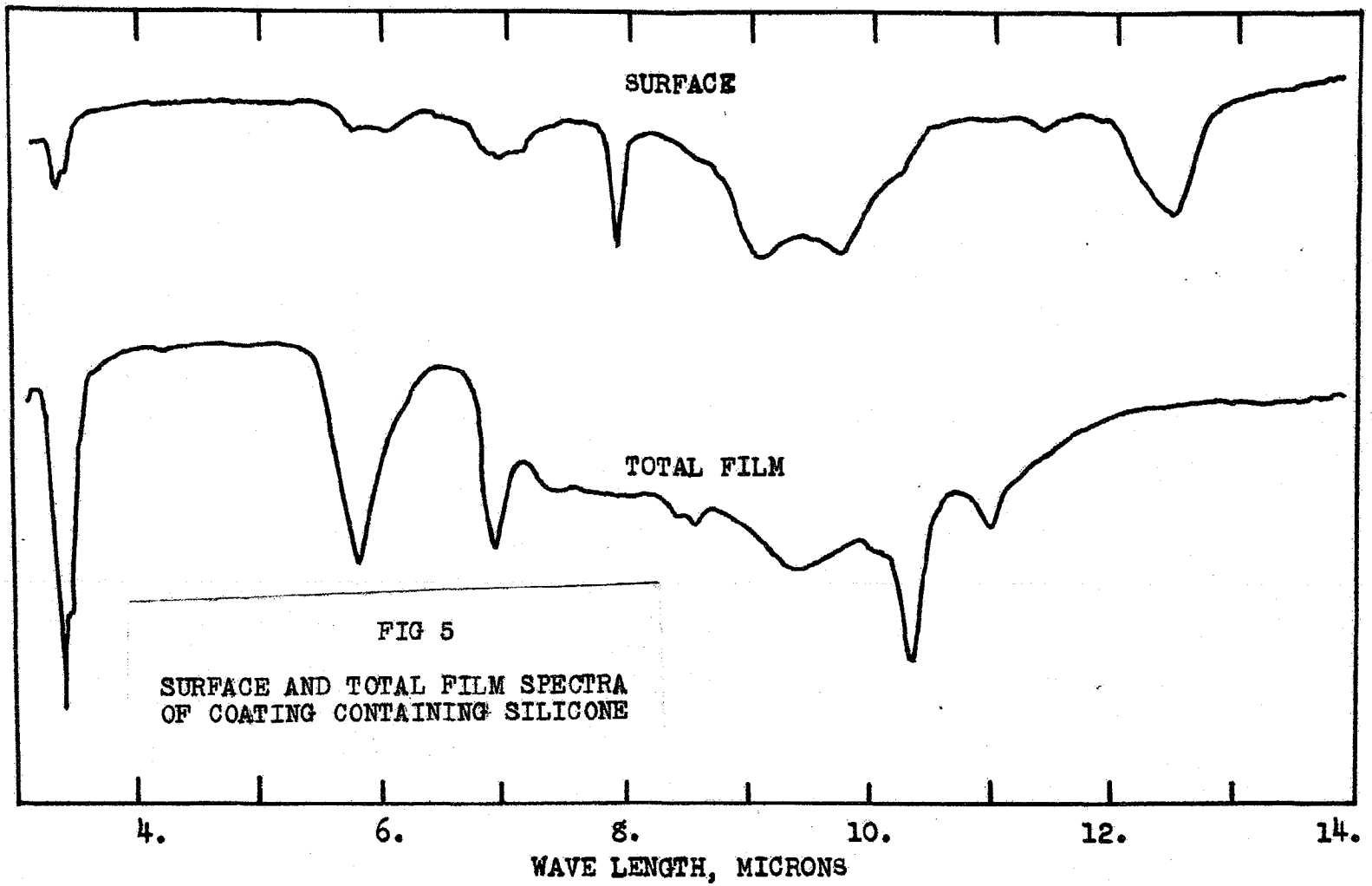


FIG 5

SURFACE AND TOTAL FILM SPECTRA
OF COATING CONTAINING SILICONE

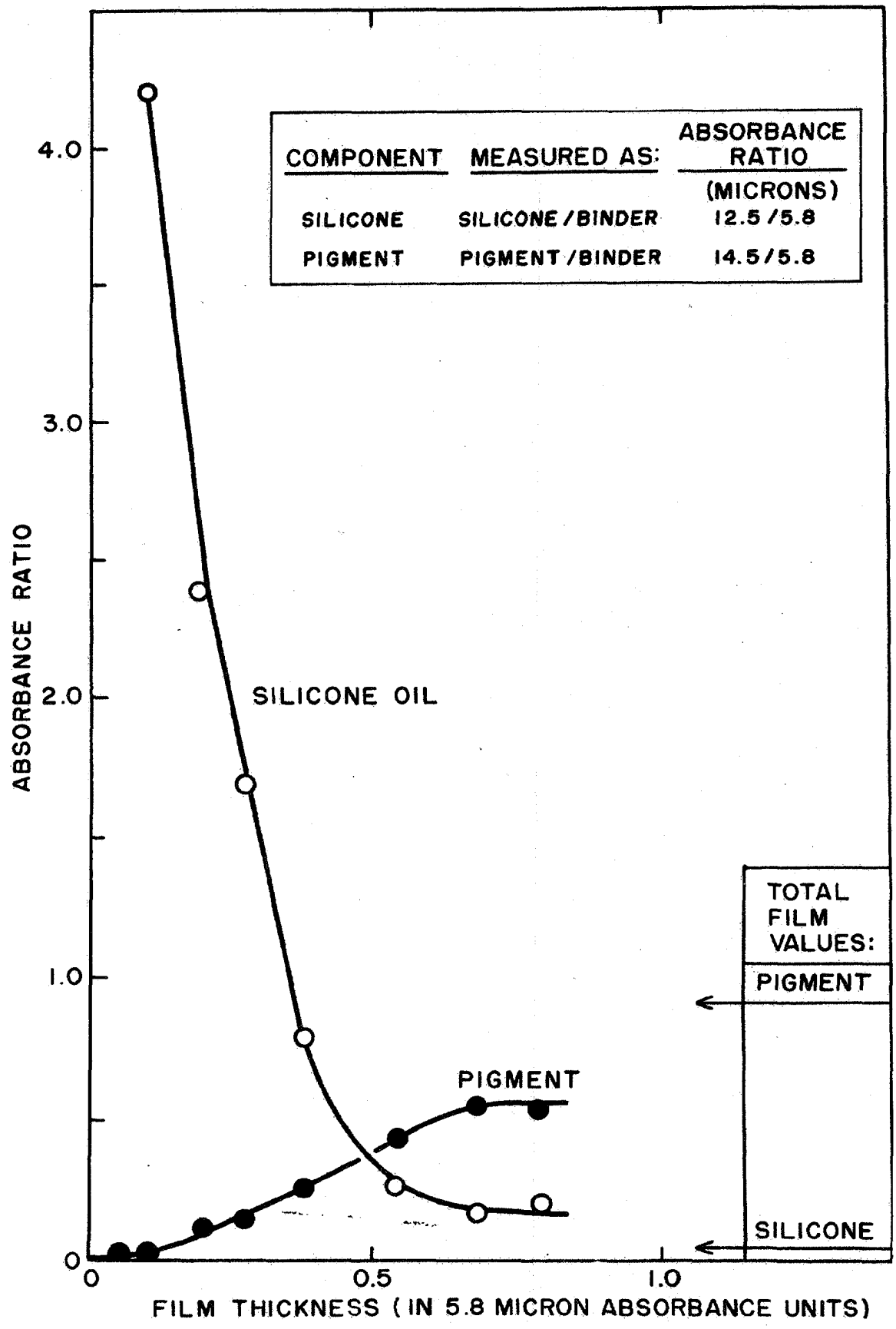


FIGURE 6. THE DISTRIBUTION OF PIGMENT AND SILICONE OIL NEAR THE SURFACE OF A PAINT FILM.

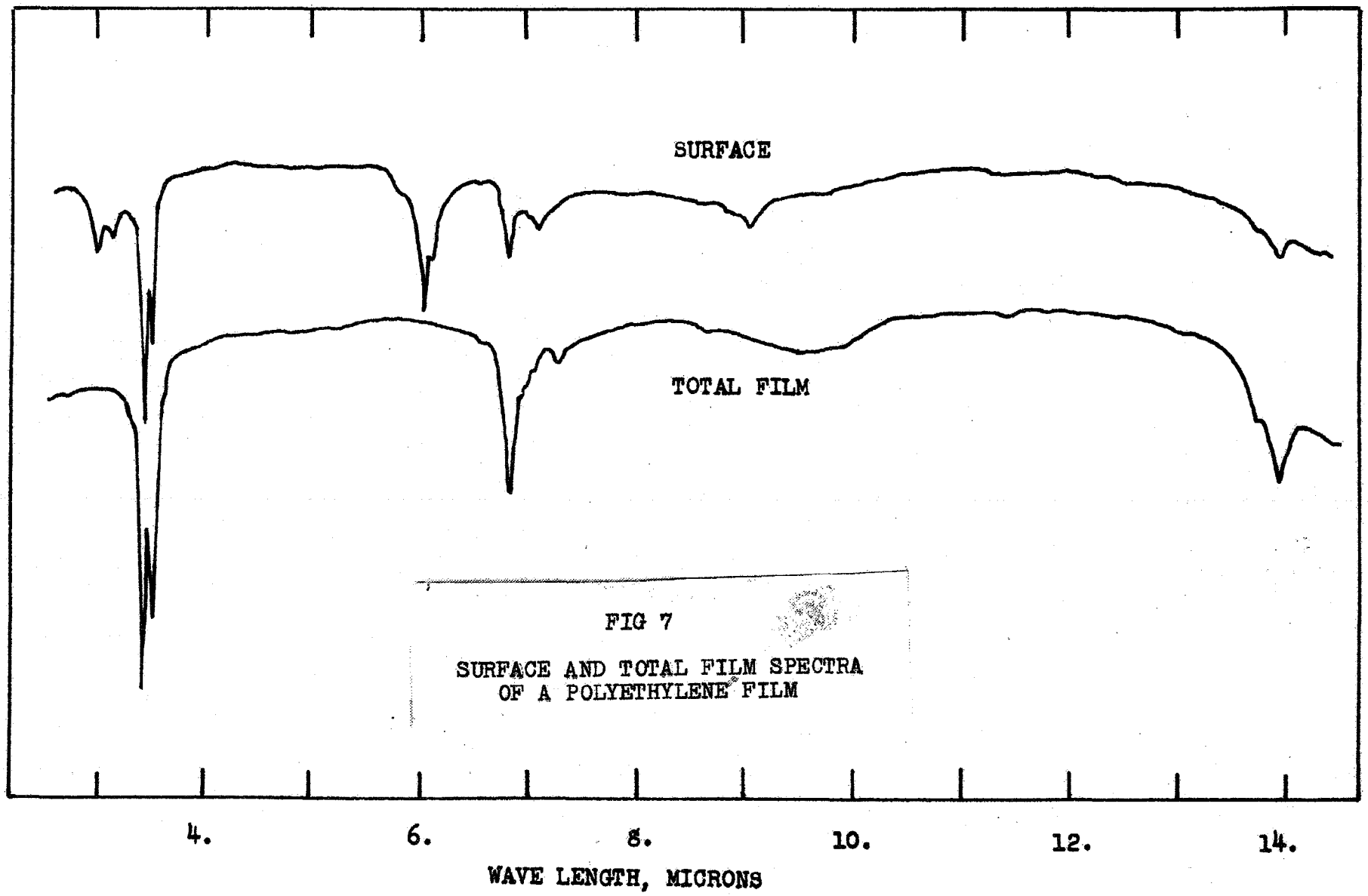
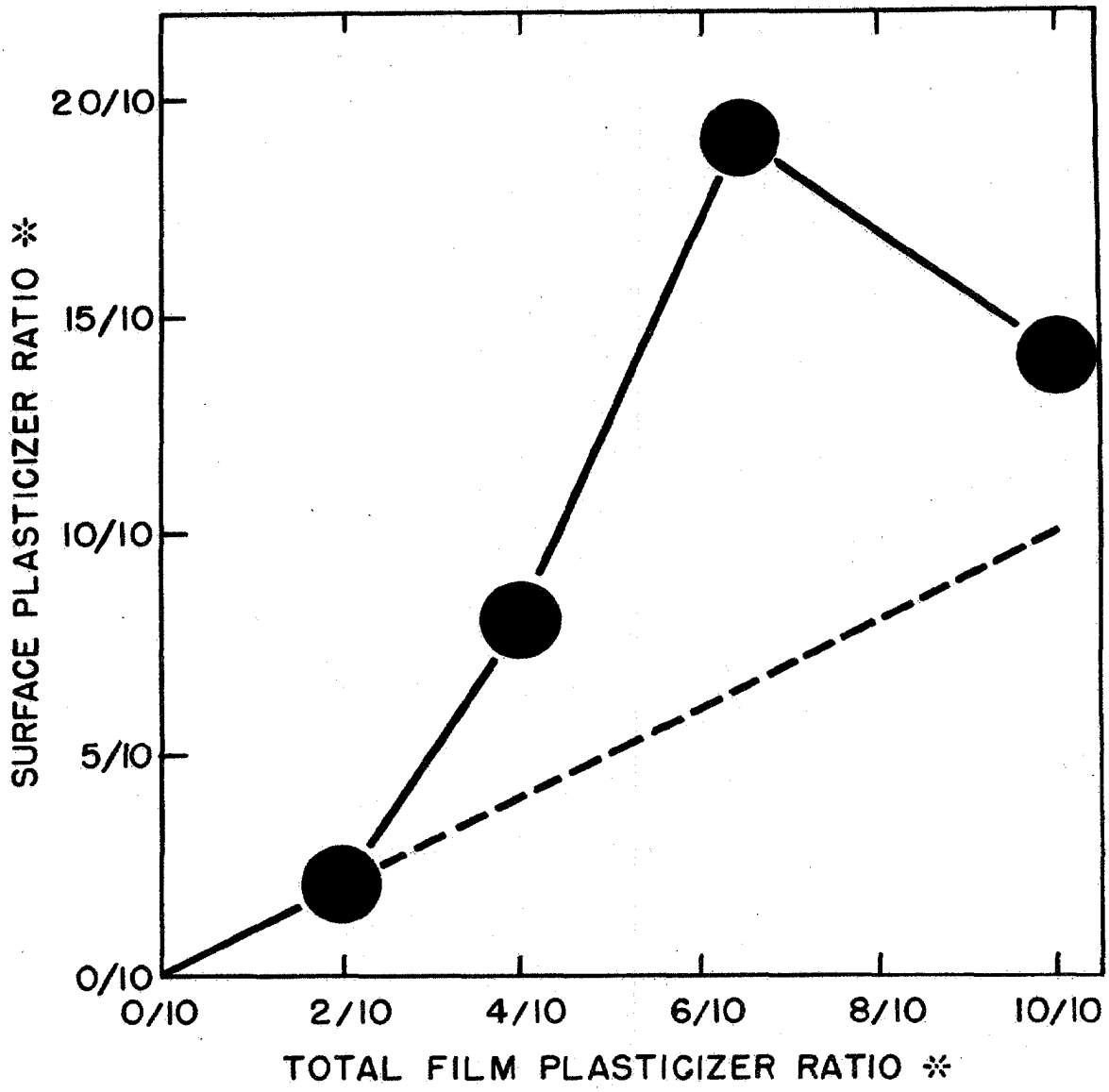


FIG 7

SURFACE AND TOTAL FILM SPECTRA
OF A POLYETHYLENE FILM



* PLASTICIZER / POLYMER RATIO MEASURED AS THE ABSORBANCE RATIO 7.9/8.4 (MICRONS).

FIGURE-8 THE CONCENTRATION OF PLASTICIZER AT THE SURFACE OF A PAINT FILM – AT VARIOUS TOTAL FILM PLASTICIZER LEVELS.