# Topographic Orientation on Buffed Polymeric Substrates: the Mechanism of Wax Buffing

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## Synopsis

This paper reports on the observation that buffed waxy polymers control the orientation of a vapor-deposited material subsequently deposited thereon. The insight into the mechanism of the buffing process of waxy polycrystalline polymers that these observations provide is presented. When a polycrystalline waxy polymer is buffed, grooves are formed. The dimensions of the grooves on the waxy polymer surface are substantially finer than the dimensions of the fibers of the buffing cloth. It is proposed that the buffing process stretches the polymer sufficiently to cause fibrillation, which results in the fine grooves observed. The fine grooves provide the topography necessary for orientation of the material deposited thereon.

## INTRODUCTION

Rubbing or buffing techniques to produce alignment are of great practical interest because of the ease of producing large aligned areas. Alignment of pigments by polishing a substrate with an abrasive powder was first examined in 1928.[1] More recently, Smith and Flanders,[2,3] have demonstrated that lithographically produced periodic surface topographical grooves in an amorphous substrate can be used to control alignment of some crystalline materials on amorphous substrates.

In the course of examining alternative methods for producing an aligned optical storage medium,[4] we discovered that unidirectional buffing of an amorphous substrate with a wax was a simple means of circumferentially aligning a squarylium (Fig. 1) pigment vapor deposited thereon. We found that vapor-deposited squarylium pigments can be aligned by two additional topographical alignment techniques. They can be aligned by vapor deposition on holographic gratings[2] and they can be aligned by vapor deposition on obliquely deposited silicon oxide films.[5] Because the wax buffing process is simple, applicable to a wide variety of substrates, amenable to low-cost fabrication, and effective in producing a high pigment orientation, it was selected for detailed examination.

From the study of the efficiency of orientation of the vapor-deposited pigment on holographic gratings, it is clear that alignment occurs only if the groove spacing is less than 500 nm. For example, pigment deposited on 1-$\mu$m gratings shows no alignment. On holographic gratings with groove spacings as fine as 333 nm, less than 50% of the vapor-deposited pigment is oriented, yet on wax-buffed substrates more than 70% of the pigment orients. This strong alignment capability of the unidirectionally buffed wax substrate suggests that the buffing process produces groove spacings finer than 333 nm. Scanning electron microscopy (SEM) indeed confirms these

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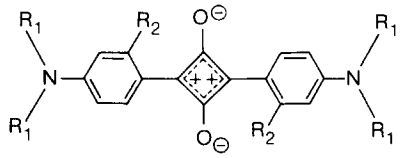

| | |
|---|---|
| $R_1 = CH_3$, $R_2 = H$ | Squarylium (SQ) |
| $R_1 = R_2 = CH_3$ | Methyl Squarylium (MeSQ) |
| $R_1 = CH_3$, $R_2 = OH$ | Hydroxy Squarylium (OHSQ) |
| $R_1 = C_2H_5$, $R_2 = OH$ | Ethylhydroxy Squarylium (EtOHSQ) |

Fig. 1. Structure of squarylium.

spacings (Fig. 2a). These narrow spacings were attained by buffing the substrate with either of two types of buffing cloths with similar results. One was a cotton buffing cloth whose smallest fiber dimension was of the order of 3$\mu$m. The other was a lint-free polyester cloth, for use in clean

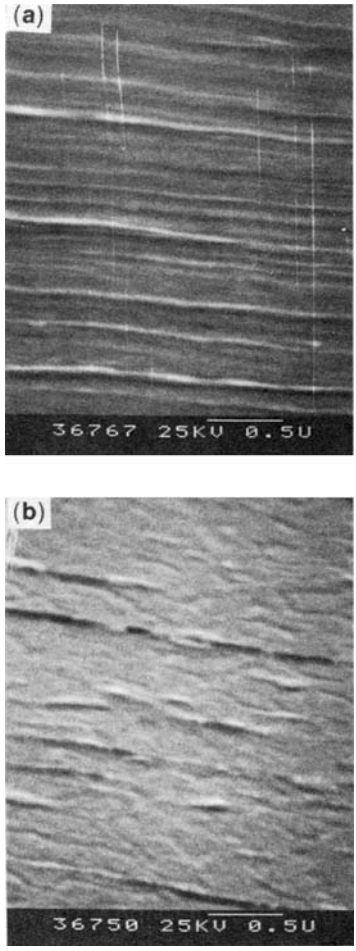


Fig. 2. SEM of surface buffed with PF-190 wax; a) after buffing; b) after heating above softening temperature.

rooms, whose narrowest fiber dimension was about 10 μm (Fig. 3). The question this paper addresses is by what mechanism do the submicrometer grooves in the wax film form in the process of being buffed by coarse fibers an order of magnitude larger than the groove spacing.

## EXPERIMENTAL

The procedure for fabricating oriented pigment films was as follows:

1. The substrate surface to be covered was polished with a wax-impregnated cloth, using a rotary motion to distribute the wax uniformly over the surface. Care was required not to have excess wax on the surface of the cloth. Too much wax produced unsatisfactory orientation. Two cloths were tried, and both were found to be satisfactory. One was conventional cotton batting, and the other was Absorbond (Texwipe), a lint-free polyester wipe cloth.

2. The surface was then buffed unidirectionally with the cloth held stationary. Repeated buffing with the buffing cloth produced no greater pig-

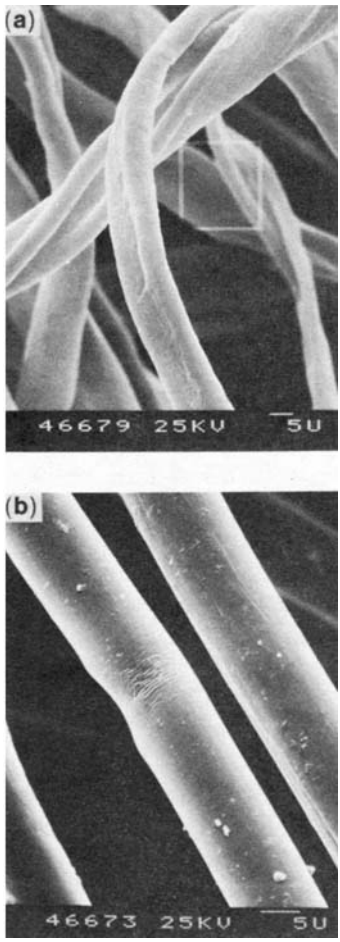


Fig. 3. SEM of fibers; a) cotton; b) polyester.

ment orientation than after the first buff wipe. The speed of buffing for a disk was of the order of 150 rpm for a 8-in. disk (150 cm/s).

3. The buffed substrate was placed in a suitable holder in a vacuum chamber. The substrate was situated appropriately to allow vapor deposition of the pigment in the ceramic boat at normal incidence.

4. The vacuum system was a small Varian V-10 bell jar system with two quartz crystal monitors and two thermal heating stations. The chamber was evacuated to a pressure of less than $10^{-4}$ torr and then the ceramic boat was heated by a coil situated directly above and in close proximity to the dry pigment powder in the boat. Heating the pigment powder from above allowed the hottest pigment molecules to evaporate and prevented excess decomposition of the powder remaining in the boat.

5. Heating was controlled such that a pigment deposition rate was maintained at about 0.1 nm/s to a film thickness of about 100 nm. Deposition at faster rates produced pigment decomposition. To deposit a pigment film on a buffed disk, the disk was rotated within the vacuum chamber at a rate of about 2 rpm past the sample position during deposition.

A variety of commercially available waxes were found to work effectively. Among these were such waxes as Eftofine FT-600F (Dura Commodities), Slipit 230 (Western Petrochemicals), and Polyfluo PF-190 (Micro Powders). The last mentioned wax was the most effective. It is reported to be a blend of low-density polyethylene and polytetrafluoroethylene. For our studies of optical storage in oriented pigment films,[4] vacuum-deposited polyethylene (MW, 1000–2000) was found to produce results about as good as the waxes. Thin (150-nm) uniform films of polyethylene could be deposited and buffed without leaving residual particle debris.

## RESULTS

To determine whether the buffing process caused the orientation of the pigment, a series of experiments was performed. If, for example, the effect was in the topography, then alignment should decrease as the wax is heated to its softening temperature (after buffing but prior to vapor deposition of the pigment). Accordingly, a series of 1 in. glass substrates was unidirectionally buffed with PF 190 and annealed for varying lengths of time at various temperatures up to its reported softening temperature (121–132°C). About 25 nm of hydroxysquarylium was subsequently evaporated on these substrates. The orientation ratio $S$ was determined by measuring the transmittance of the film at its peak with light polarized parallel and perpendicular to the buffing direction.[4,6]

The results are shown in Figure 4. The experiment was then repeated with a polytetrafluoroethylene wax, Vydax 1000 (du Pont), with a much higher softening temperature (322°C). The results are shown in Figure 5.

It is evident that the orientation of the pigment decreases with increasing annealing temperature of the buffed wax surface up to the softening temperature of the particular wax used. SEM of the buffed and annealed surface compared with the buffed, unannealed surface reveals a distinct loss in the high-frequency (narrow) grooves in the wax when heated to its softening temperature (Fig. 2b).

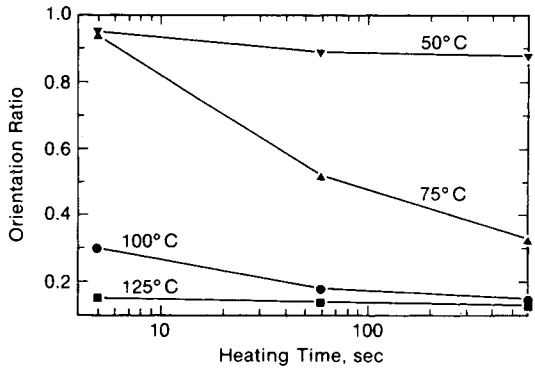


Fig. 4. Orientation ratio *versus* time (at temperatures) for OHSQ/PF-190.

Another test of a purely topographical effect rather than an epitaxial deposition on oriented microcrystals of the wax would be whether the buffed wax surface would align molecules other than the squarylium pigments. The molecules that were selected were limited to those that could be vapor deposited and were likely to be dichroic. A few of the molecules that orient on the buffed wax surface are shown in Figure 6. These are molecules with little similarity among the functional groups, yet they orient similarly on the buffed wax surface.

## DISCUSSION AND CONCLUSIONS

As noted in the introduction, the main concern is to explain by what mechanism are submicrometer grooves formed on the surface of the wax with buffing cloths whose smallest fiber dimension is an order of magnitude larger than the grooves. The suggested hypothesis is that the buffing process creates a high shear stress on the surface of the wax. This high shear stress draws the waxy polymer. If the polymer is partially crystalline, it will have some tendency to fibrillate on drawing. Fibrillation and polarized infrared (IR) bands are normally observed in drawn high-molecular-weight polymers.[7]

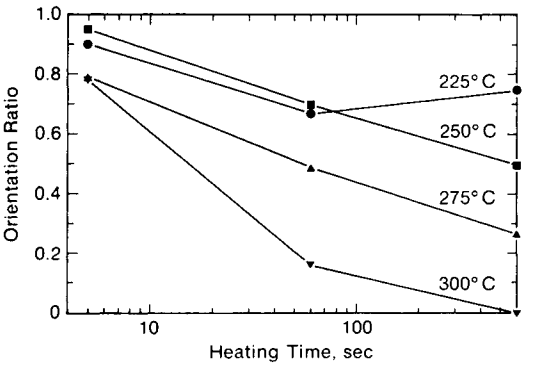


Fig. 5. Orientstion ratio *versus* time (at temperautres) for OHSQ/Vydax-1000.

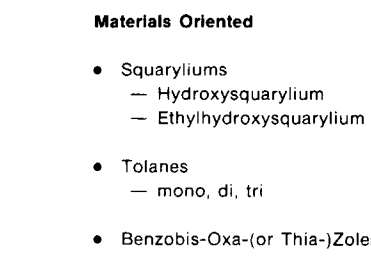


Fig. 6. Materials oriented.

If fibrillation also occurs in these buffed low-molecular-weight polycrystalline polyethylene and polytetrafluoroethylene waxes, then dichrosim in the polarized IR bands of the buffed wax layer should be observed. These films are so thin only the most intense IR bands are observed after buffing. The intense bands in polyethylene are not dichroic but those in tetrafluoroethylenes are. A low-molecular-weight fluorotelomer wax (Vydax AR, du Pont) was therefore selected for this study. This fluorotelomer, which has a molecular weight of about 3700, was vapor deposited (60 nm) on a NaCl plate in a vacuum of $< 10^{-4}$ torr. This vapor-deposited fluorotelomer is one of the wax films known to orient the vapor-deposited pigments after buffing. The unpolarized FTIR absorption spectrum (Fig. 7) of the unbuffed film showed the characteristically intense CF asymmetric and symmetrical stretching vibrations at 1210 and 1155 $cm^{-1}$, respectively. These bands are polarized *Normal* to the polymer chain axis and would therefore exhibit a more intense absorption in the direction *Perpendicular* to the buffing direction. The polarized FTIR spectrum of this film after unidirectional buffing is shown in Figure 7b (with the baseline shifted for ease of comparison). It is clear that the absorption *Perpendicular* to the buffing direction is the more intense. The ratio of perpendicular to parallel absorbances at 1150 $cm^{-1}$ is 1.9 and at 1210 is 1.6, which corresponds to an alignment of about 20% of the chains after buffing.

If fibrillation of the buffed wax produces the submicrometer grooves necessary for topographical alignment of pigment, then it ought to be possible to align the pigment on a drawn high-molecular-weight polymer that fibrillates.

This experiment was performed by taking a sheet of undrawn low-density polyethylene film (low-density polyethylene tubing for packaging, made by Dana Films) and drawing it to varying draw ratios. The surface of the film was not touched or treated in any way after drawing. A section of the drawn film was placed in the vacuum chamber, and hydroxysquarylium was vapor deposited thereon. The orientation ratio of the deposited pigment was determined and the results plotted against draw ratio for two different draw rates. The results are shown in Figure 8. The undrawn film showed no pigment orientation, but the drawn films showed increasing degrees of orientation. SEM (Fig. 9) of the highly drawn, unetched surface showed grooves parallel to the draw direction, with groove spacing as small as 125

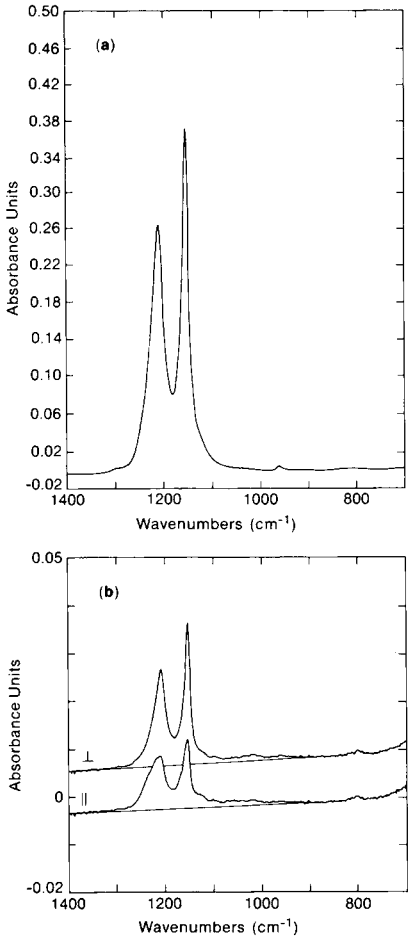


Fig. 7. Polarized FTIR spectrum of Vydax AR; a) before buffing; b) after buffing.

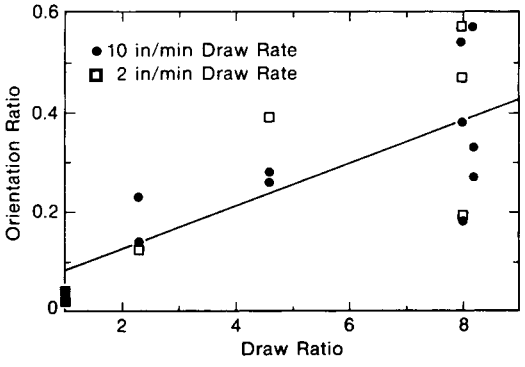


Fig. 8. Orientation ratio *versus* draw ratio for low density polyethylene film.

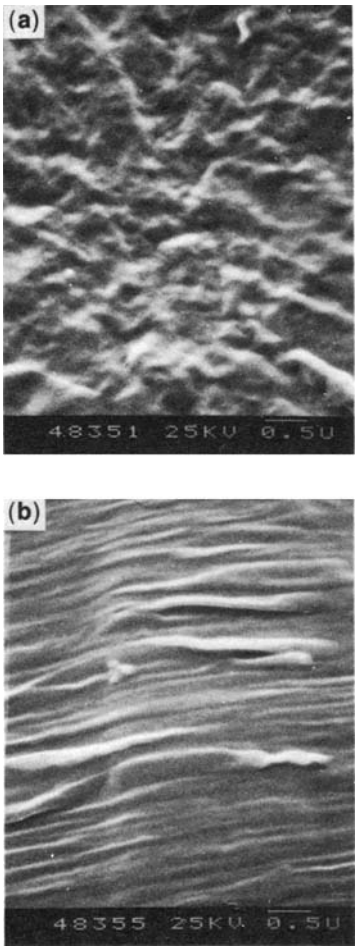


Fig. 9. SEM of unetched low density polyethylene film surface; a) as received; b) after drawing (@ draw ratio of 8:1)

nm. For comparison (Fig. 2a), the groove spacing in buffed waxy polymer films are as small as 80 nm.

From this study we conclude that the process of buffing a polycrystalline wax results in stretching and fibrillating a very thin (about 30 nm) film of the wax over the surface being buffed. This produces a tougher surface than is attained when a wax is just rubbed on the surface. Using too much wax on the buffing cloth reduces the friction between the buffing cloth and the surface films and interferes with the stretching and fibrillation process. The resulting fibrils are so fine that they can be used to topographically align molecules. This is a simple and low cost means of obtaining large aligned areas of materials.

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