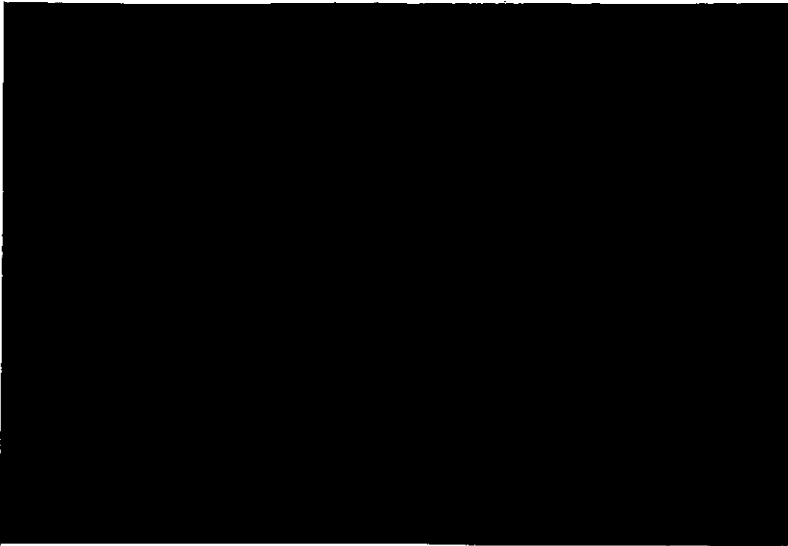


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ON PARTICLE TRACK DETECTORS*

by

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I. STUDIES ON THE ETCHING OF POLYCARBONATE FILM
BY AQUEOUS SODIUM HYDROXIDE

Abstract

Aqueous sodium hydroxide is widely used to develop charged particle tracks in polycarbonate film, particularly Lexan. The chemical nature of the etching process for this system has been determined. The principal, soluble organic etch product is the anion of Bisphenol A. The etch product which separates as a precipitate is simply the disodium salt of Bisphenol A. No evidence was found for the existence of polymeric species either in solution or in the precipitated phase. If relatively large amounts of polycarbonate are decomposed, the anion of phenol may also become a significant soluble etch product. The nature of the soluble components of the etching solution becomes more complicated with increasing age as a result of air oxidation.

A method employing ultra-violet absorbance was developed for monitoring the concentration of the etch products in solution. Using this method it was possible to study the formation of the etching solution saturated in etch products. It was found that the system super-saturates to a significant extent before precipitation occurs. It was also learned that the system approaches its equilibrium state rather slowly. It is felt that both these phenomena may be due to the presence of surfactant in the solution. In light of these findings, suggestions are given regarding the preparation and maintenance of the saturated etch solution.

Finally, studies were performed on the influence of etch solution composition on the bulk etch rate. The results suggest that the nature of the components present is important not only in yielding a uniform etch but also in providing an etching solution in which the bulk etch rate and the uniformity of the etch are not greatly dependent on the degree of agitation of the solution. The combination of Dowfax 2A1 surfactant and saturated Bisphenol A gave the most satisfactory behavior by the above criteria.

Introduction

The bulk etch rate of Lexan polycarbonate film in aqueous sodium hydroxide was found by Peterson^[1] to depend significantly on the concentration of the products of the etching process. Smooth particle track profiles were obtained only when using an etchant saturated with the etch products. The purpose of this work was to investigate the chemical composition of this etching solution. This information can be used to develop methods for monitoring etch product concentration and may lead to a route for preparing a "synthetic" saturated etchant thus offering an alternative to the time consuming procedure presently used (etching sheets of polycarbonate until saturation is achieved).

Knowledge of the chemical components of the etching solution also allows a determination of their individual effects on the bulk and track etch rates. It is hoped that studies of this type will lead to a more fundamental understanding of the bulk and track etching processes.

The work presented here will be divided into three parts. The first will deal with the determination of the chemical composition of the etch products and the possibility of a synthetic etchant. The second will present a method for monitoring the concentration of etch products together with the results of monitoring a working etch bath. The final part gives the results of some bulk etch rate studies in which the effects of individual components of the etch solution were tested.

PART 1. CHEMICAL COMPOSITION OF THE ETCH PRODUCTS

A. Experimental Procedure

Natural Lexan film (Grade 8070-112) was used in the experiments. It is an extruded product containing no plasticizers or other additives.^[2] Weighed samples of Lexan were reacted with 6.25 N NaOH in polyethylene bottles held at $40.0 \pm 0.1^\circ\text{C}$ in a shaker bath. Isolation of the dissolved organic components of the reaction mixture was achieved as follows. Samples were withdrawn with a 50 ml pipette fitted with a "medium" fritted-glass filter. This insured that no suspended matter was obtained. The sample was titrated in an ice-bath with 12 M hydrochloric acid to the methyl orange end-point ($\text{pH} = 4$) and then extracted successively with 25 and 15 ml portions of diethyl ether. The extract was dried with anhydrous sodium sulfate and the ether removed by evaporation. Based on experiments using weighed amounts of etch products this extraction procedure is at least 99% efficient.

The precipitated products were isolated by filtering a sample of the suspension, dissolving the solid obtained in water, and then extracting the organic components as described above. The ready solubility of the precipitated etch products in water (as opposed to 6.25 N NaOH) allowed an easy separation of them from the flakes of unreacted Lexan also found to be present.

Study of the ultra-violet absorption of the etch products was performed on Beckman Model DK-2A and Beckman Model DU spectrophotometers (the latter being used for the analytical work). Measurements were made using matched

1 cm quartz cells, one of which contained the appropriate reagent blank. Generally 1 ml samples were withdrawn with a pipette fitted with a "medium" fritted-glass filter and a dilution of 1:100 with distilled water made before measurement.

Infra-red spectra of the solids in Nujol mulls were taken on a Perkin-Elmer Model 337 spectrophotometer.

Practical grade 4,4'-iso-Propylidenediphenol (Bisphenol A) obtained from Eastman Organic Chemicals was recrystallized from 90% toluene, 10% iso-Butyl-alcohol. The melting point of the recrystallized material was 156-157°C compared to 152-156°C for the practical grade.

B. Experimental Results

Samples of the dissolved organic components of the reaction mixture were obtained just after the mixture reached saturation and later at the point where the plastic was almost completely decomposed. The solids obtained at saturation were slightly off-white, had no appreciable odor, and melted at 155-156°C. The infra-red spectra of these solids exactly matched that of Bisphenol A. Samples taken when the plastic had all decomposed yielded yellow colored solids having a strong phenolic odor and broad melting ranges, e.g., 130-145°C. Thin layer chromatography of this material using silica gel (0.20 mm) on aluminum with chloroform as solvent demonstrated the presence of phenol as the major impurity. The chromatographic procedure was essentially that of Zowall and Lewandowska^[3] except that the chromatograms were viewed under ultraviolet light instead of using a developer. A very minor component(s) with small R_f value was also noted but not identified.

Samples of the precipitated phase of the reaction mixture always gave

white, odorless solids, melting at 156-157°C and having the same I.R. as Bisphenol A.

A typical ultra-violet spectrum of the dissolved etch products and that of Bisphenol A in alkaline solution are shown in Fig 1. They corresponded quite closely except for the peak near 240 nm which in the case of the etch products broadened and shifted slightly to shorter wavelengths as more Lexan was decomposed. This variation can be explained by the known presence of phenol in the aqueous phase. The spectrum of phenol in alkaline solution^[4] has peaks at 287 and 235 nm.

The ultra-violet absorbance of Bisphenol A in alkaline solution was used to determine its solubility limit under the experimental conditions. The peak at 293 nm was chosen for the analytical work as constituents of the reaction mixture such as carbonate ion and hydroxide ion have much less absorbance here than at 243 nm. Solutions of Bisphenol A showed excellent adherence to Beer's Law and yielded a value of 23.3 ± 0.3 l/g cm for the absorptivity in 0.0625 N NaOH. This data allowed a determination of the solubility of Bisphenol A in 6.25 N NaOH at 40°C. It was found to be 0.72 ± 0.02 g/l.

Measurements of the 293 nm absorbance of the saturated etch products always gave a reading higher than that expected for saturated Bisphenol A. The specific value depended on the amount of Lexan plastic that had been degraded and on the age of the solution. The presence of phenol can explain both these observations. Phenol is readily soluble in sodium hydroxide solutions compared to the relatively insoluble Bisphenol A. The concentration of Bisphenol A becomes constant at its saturation point but the concentration of phenol continues to increase as more plastic is decomposed. Phenol in alkaline solution may

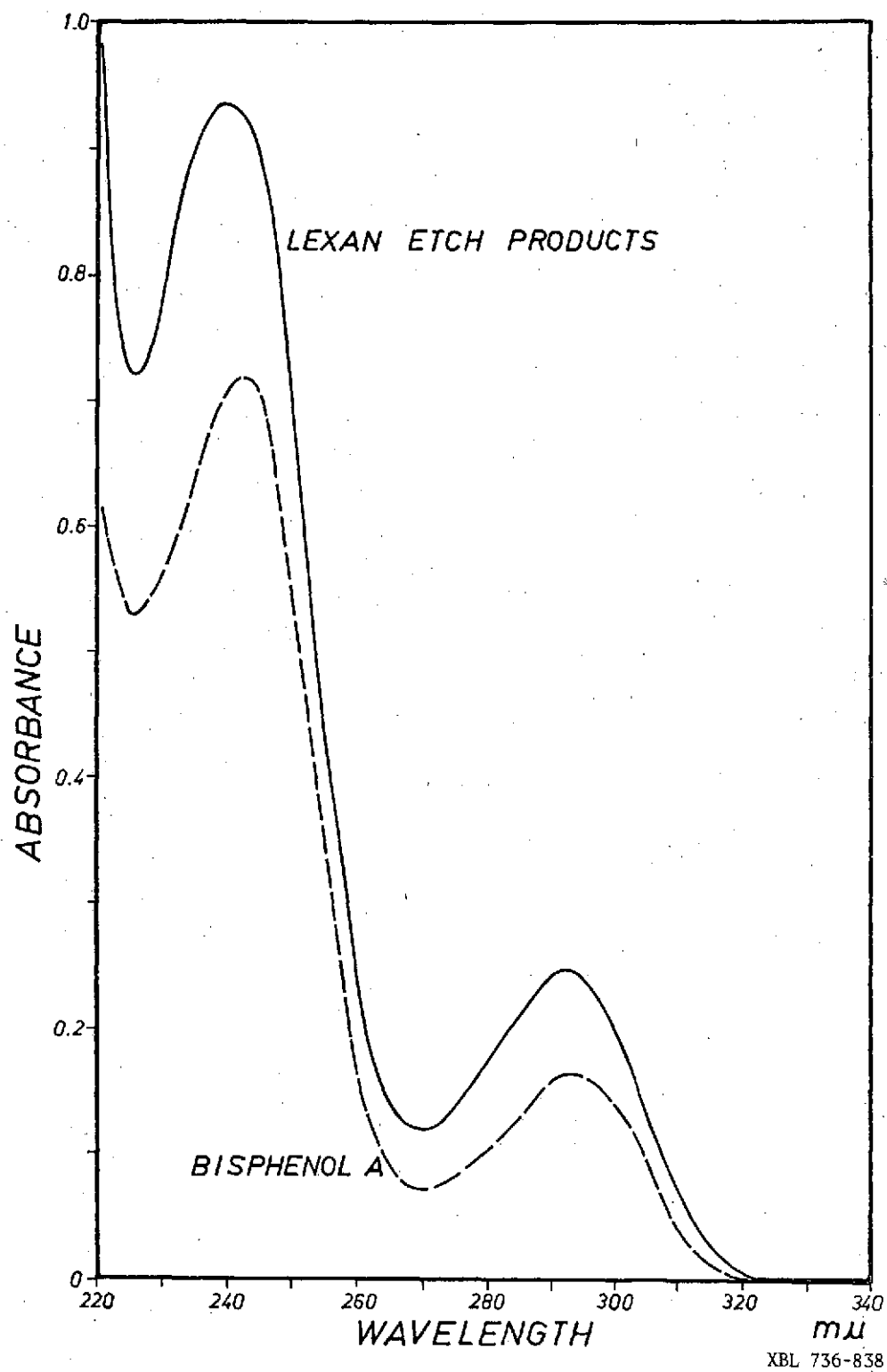
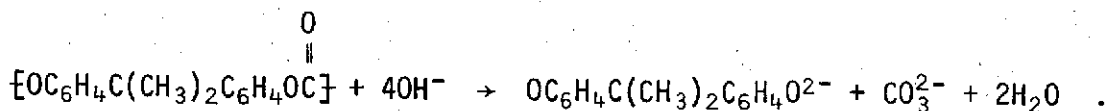


Figure 1. Typical spectrum of Lexan etch products and that of Bisphenol A. Samples were withdrawn from their respective saturated solutions in 6.25 N NaOH and diluted 1:100 with distilled water before measurement.

be air oxidized to quinone type compounds which have an intense yellow color. The solutions of etch products were observed to develop a yellow tint with age thus resulting in an increased absorbance reading. The oxidation or decomposition of organic components other than phenol may add further complications to the monitoring of aged solutions. When 6 g/l of Lexan were decomposed under the conditions mentioned in the experimental procedure, noticeable yellowing occurred after about two months. In practice the development of the yellow color will depend on the amount of polycarbonate etched, the temperature, and those factors controlling the accessibility of oxygen to the etchant.

C. Discussion

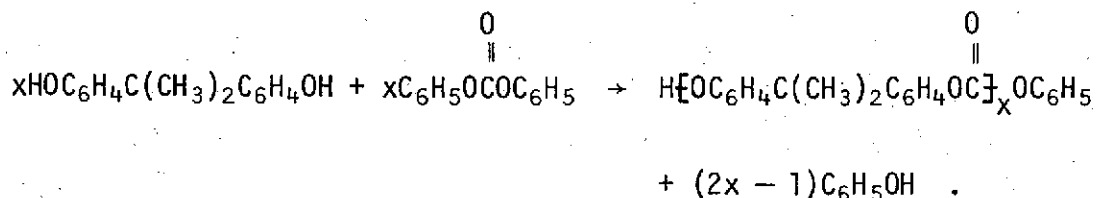
The principal reaction in the etching of Lexan polycarbonate plastic by aqueous sodium hydroxide appears to be



After sufficient reaction has occurred, a precipitate of the disodium salt of Bisphenol A is formed. It is believed that the reaction yields exclusively the monomeric species since infra-red spectra of the soluble and the precipitated etch products show the complete absence of the strong absorption at 1775 cm^{-1} which is characteristic of the carbonate group in the polymer.

The primary organic component in the aqueous phase of the etch products other than Bisphenol A is phenol. The presence of phenol may arise in several ways. First, phenol is an impurity in practical grade Bisphenol A which is

used to produce Lexan. In the case of polycarbonates produced by the phosgenation method, this is probably the only source of phenol. However, another general method for making Lexan is by the ester exchange synthesis^[5]



The presence of unreacted diphenylcarbonate or phenol product would give rise to phenol in the etching solution. Hydrolysis of the chain terminating group

$$\begin{array}{c}
 \text{O} \\
 \parallel \\
 \text{OCOC}_6\text{H}_5
 \end{array}$$
 would also produce phenol.

Additional organic components may arise from those high-boiling impurities normally found in practical grade Bisphenol A^[6] although these would be expected to be minor. The amount of each organic component in the etching solution would depend on the amount of plastic that had been decomposed and on the relative solubilities of the compounds concerned.

D. Preparation of a "Synthetic" Saturated Etchant

Saturated etchant can be prepared simply by adding the required amount of Bisphenol A to the sodium hydroxide solution. It should be noted, however, that Bisphenol A dissolves very slowly in 6.25 N NaOH unless it is very finely divided and stirred vigorously. An effective method to achieve saturation consisted in dissolving Bisphenol A in the minimum amount of methanol and adding this solution dropwise to well-stirred sodium hydroxide solution. The amount

of methanol required is only about 0.2% of the volume of the final solution. Another procedure is to grind Bisphenol A into a fine powder and to form a paste of it with Dowfax 2A1^[7] surfactant and sodium hydroxide followed by addition to rapidly stirred sodium hydroxide solution. It was found that unless great care is taken the above methods do not always result in a truly saturated solution. It is felt that the use of the disodium salt of Bisphenol A to form the saturated solution would be much more satisfactory given its ready solubility in water. We are currently trying to develop a convenient preparation of the disodium salt so that this idea may be tested. Phenol does not present this difficulty as it is readily soluble in sodium hydroxide solution.

PART 2. UV MONITORING OF THE ETCH BATH

A. Experimental Procedure

The etch bath was a rectangular, polyethylene tank having a tight fitting Plexiglass cover. The etchant consisted of 74 liters of 6.25 N NaOH and 0.045% Dowfax 2A1 surfactant (by volume). The etchant was kept well-stirred and maintained at 40.0°C. To achieve a solution saturated in etch products, sixteen 12 x 16 inch sheets of Lexan (usually 7-10 mil thick) fitted on a Plexiglass rack are placed in the etch bath and left in until the cloud-point.

Monitoring of the etch bath solution began when the Lexan sheets were added to the bath (time "zero").

One milliliter samples were withdrawn from the etch bath using a pipette fitted with a Pyrex brand fritted filter. The filter was of the "medium" designation having a maximum pore size of 10-15 microns. The filter was attached to the pipette by means of a short length of polyethylene tubing. Suction from a water aspirator aided in obtaining the samples.

The sample was diluted 1:100 with distilled water and its absorbance at 293 nm and 243 nm measured against a reference blank. The blank was a 1:100 dilution of 0.045% Dowfax 2A1-6.25 N NaOH solution.

Beckman DU and DK-2A spectrophotometers were used for the absorbance measurements. The latter instrument allows the automatic recording of the entire UV spectrum of the etch products.

B. Experimental Results and Discussion

Two separate etch bath set-ups were monitored. The results are shown in Figures 2 and 3.

The behavior of the etching process up to the point of precipitation is rather simple. The rate probably depends principally on the surface area of the Lexan and the rate of stirring for a given temperature and etchant concentration. The ratio of slopes in this region, Fig. 2/Fig. 3, is 1.9. The rate of stirring for the January-March 1973 set-up was 160 rpm; the rate of stirring for the 1972 set-up was not measured exactly but is estimated to have been in excess of 250 rpm. The linearity in this region suggests that the surface area of the Lexan sheets does not change radically with etching although it is possible that the predominant factor in determining the rate is the rate of stirring.

In both of the experiments the absorbance at 293 nm reaches about 0.30 before precipitation occurs. This corresponds to an etch product concentration of about 1.3 g/l (based on the absorptivity of Bisphenol A, 23.3 l/g·cm) in excellent agreement with the value Peterson^[1] obtained (1.3 g/l) from observation of the cloud-point. After precipitation the absorbance at 293 nm decreases and levels off. This suggests that the etch products are in a supersaturated state prior to precipitation. The leveling off of the absorbance may indicate the establishment of a truly saturated solution. The attainment of this "equilibrium" state appears to be quite slow. It was noted in the monitoring of January-March 1973 that the cloudiness, and thus the apparent amount of precipitate, increased gradually even after the Lexan sheets were removed.

Absorbance at 293 nm

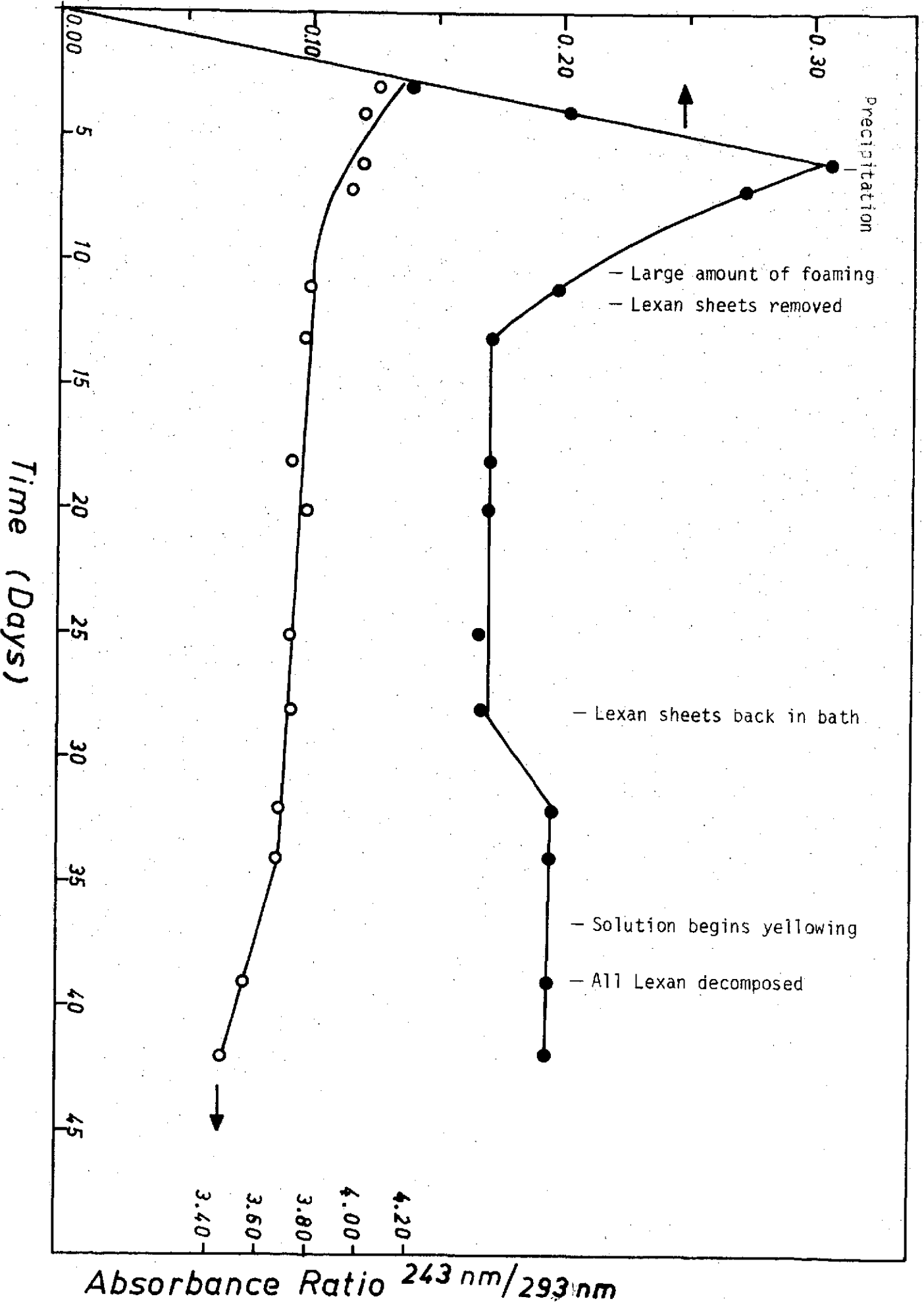


Figure 2. UV-monitoring of etch bath September-October 1972.

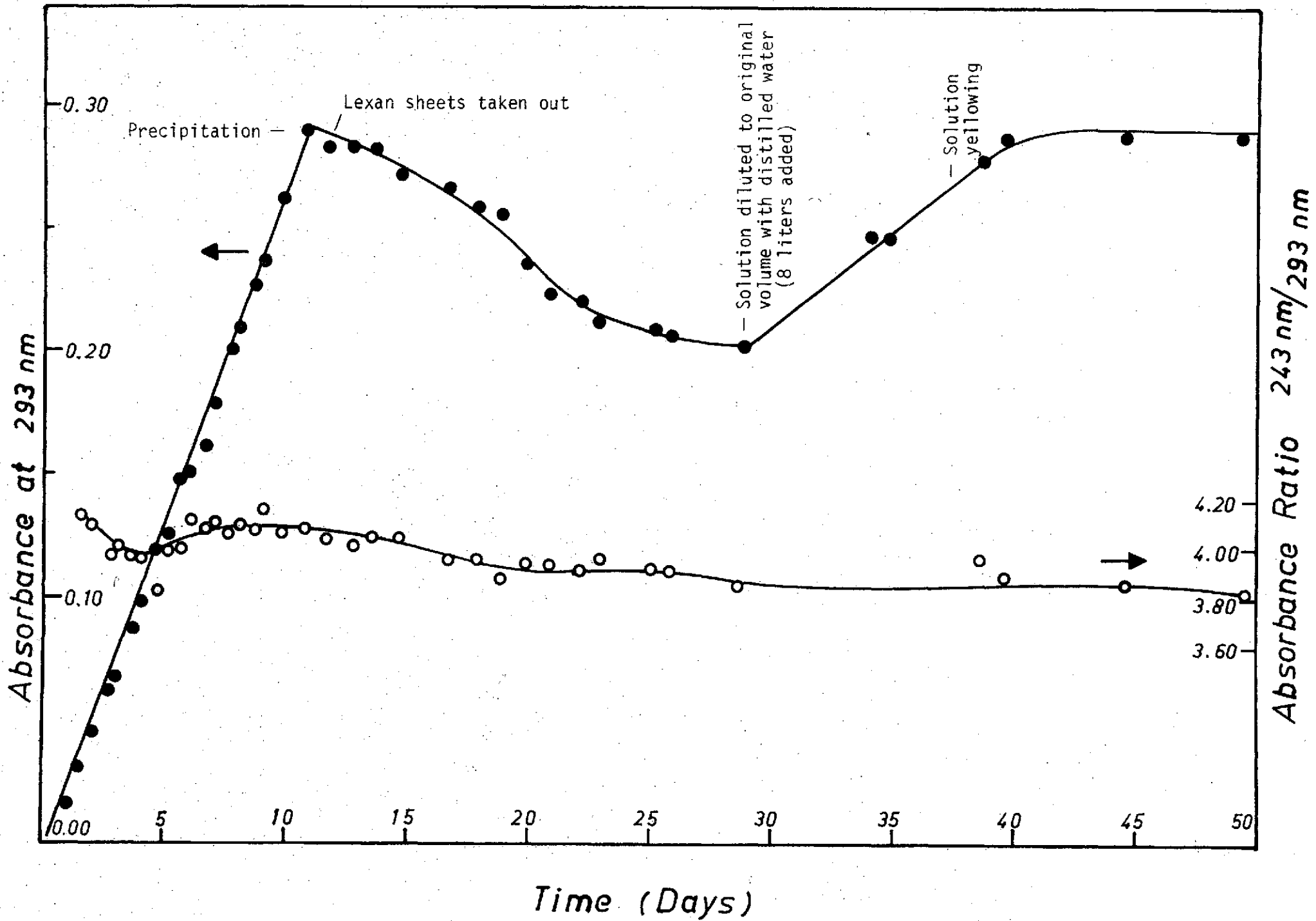


Figure 3. UV-monitoring of etch bath January-March 1973.

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from the solution. This visual effect is further evidence of the supersaturation phenomenon. The tendency of the system to supersaturate and its sluggishness in reaching equilibrium may be due to the presence of the surfactant. The surfactant molecules could form a layer on small particles of the disodium salt of Bisphenol A, thereby preventing aggregation with other small particles and thus precipitation. This "protective" effect of the surfactant is apparently good only up to an etch product concentration of 1.3 g/l under the conditions of these experiments. At this point particles of sufficient size to initiate precipitation are formed. Precipitation then ensues although it is slowed by the coating action of the surfactant.

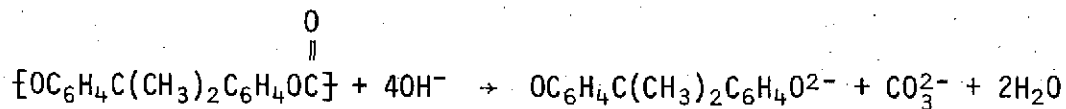
Perhaps a more satisfactory way to prepare the saturated etchant would be to hold back the addition of the surfactant until after precipitation. This might eliminate the problems mentioned above, and in addition would allow much more rapid stirring initially since there would be no problem with foaming.

The observations after the point of precipitation are complicated by several factors. First, there is the problem of evaporation. This results in an increase in the concentration of sodium ions and a consequent depression of the solubility of the principal etch product (the disodium salt of Bisphenol A) through the common ion effect. The effect of restoring the etch bath to its original volume is shown quite dramatically in Fig. 3 (29th day). This problem can easily be eliminated by maintaining the original volume of the etchant throughout its operation through the addition of distilled water. The second factor is the appearance of the phenolate ion as an etch product. The amount of this species in solution is determined by the particular batch

of Lexan used and the amount of it which is decomposed (the concentration of phenolate ion increasing as more Lexan is decomposed). This species gives rise to absorption at 293 nm in addition to that from saturated bisphenolate. A good measure of the presence of phenolate is the ratio of absorbance at 243 and 293 nm. For pure bisphenolate, the ratio is 4.1; for pure phenolate, the ratio is 2.5. As can be seen in Figures 2 and 3, the ratio starts off at 4.1 and shows a gradual decrease. The decrease in the ratio for the 1972 experiment is much greater than in 1973 because the large Lexan sheets were eventually allowed to decompose completely whereas in the latter experiment the Lexan sheets were removed from the solution at the point of precipitation. Figure 2 shows the increase in absorbance at 293 nm caused by adding additional large amounts of Lexan to the saturated etch bath (28th day). Note the corresponding decrease in the absorbance ratio. The control of this variable can be achieved by always using the same batch of Lexan (if possible) and by pulling the Lexan sheets at the point of precipitation. The point of precipitation can be predicted to within about 6 hours by plotting absorbance at 293 nm against time for a given etch-bath set-up and extrapolating to an absorbance of 0.30.

The third factor which complicates the monitoring of the etch-bath is the gradual air oxidation of the etch products (this includes both the phenolate and bisphenolate ions). The oxidation produces quinone type compounds which are highly colored. One can detect this visually as a yellowing of the solution. These oxidation products also cause an increase in absorbance at 293 nm and cause the absorbance ratio to decrease. This problem might be solved by adding a suitable reducing agent to the etch bath.

Finally, it should be noted that OH^- is consumed both in the etching process



and by absorbance of CO_2 from the air



Thus the concentration of OH^- in the bath will vary with time and use. Although this would have negligible effect on the monitoring of the organic etch products, there may be a decrease in the bulk etch rate if sufficient OH^- is depleted. The effect of CO_3^{2-} concentration on the bulk etch rate may also be worth study.

PART 3. BULK ETCH RATE STUDIES

A. Experimental Procedure

(1) Using mild agitation

These etch rate experiments were carried out using small sections of Lexan sheet (4 cm x 3 cm x 190 μm) suspended in 500 ml of etchant by means of a nichrome wire (Nickel Chrome Alloy A, Gauge 22). The etchants were contained in 500 ml, wide-mouth, Erlenmeyer flasks. These were closed off by rubber stoppers wrapped with polyethylene sheet. The rubber stoppers served as the point of attachment of the nichrome wires. The flasks and contents were kept at $40.0 \pm 0.1^\circ\text{C}$ in a shaker bath. The shaker bath had a displacement of 3 cm and was operated at 150 strokes per minute.

The progress of the etching process was followed by measuring the change in thickness of the Lexan sheets using a micrometer manufactured by B. C. Ames Company, Waltham, Massachusetts. The precision of this device is about ± 0.5 microns. This figure was established by repeated measurement at approximately the same point on a sheet of Lexan. Etch rate data were obtained by taking five readings at each of three selected points per Lexan sheet. The sheets were removed from the etchants, dipped repeatedly in distilled water and towel dried with Kimwipes before the thickness measurements were taken.

Etchants were prepared in the following manner. Etchant saturated with Bisphenol A and having a large amount of precipitate present was prepared by slowly adding a solution of 2 grams Bisphenol A in 5 ml methanol to 500 ml of

well-stirred 6.25 N NaOH. The same procedure was used to prepare saturated etchant having little or no precipitate except that 0.36 g of Bisphenol A was used. Those etchants containing Dowfax 2A1 were made having 0.045% (by volume) of the surfactant.

(2) Using rapid stirring

The procedure for these experiments was similar to that above except for the following.

The experiments were carried out using three small sections of Lexan sheet (4 cm x 3 cm x 190 μ m) suspended in 1 quart (approximately 900 ml) of etchant by means of nichrome wire. The etchants were contained in 1 quart Nalgene polyethylene containers covered by 12 cm x 12 cm squares of quarter inch plexiglass. The sheets were suspended in the solution by the nichrome wire which was attached to the sides of the containers. The containers and the contents were kept at $40.0 \pm 0.1^\circ\text{C}$ in a water bath. The etchant solution was mixed by rapid, constant stirring (400 to 500 rpm) by Nalgene polyethylene stirrers connected to Cenco motors (No. 18834).

The Makrofol KG experimental arrangement differed only in the size of the sections of sheets and the method of attachment. The sections of Makrofol KG used were approximately 3 cm x 2 cm x 20 μ m. Due to the thickness of Makrofol, it could not be suspended by hooking to the nichrome wire as was done with the Lexan. Instead, a clip fashioned out of nichrome wire was used to suspend the Makrofol KG.

Etchants were prepared in the following manner. Etchant saturated with Bisphenol A by the methanol method and having a large amount of precipitate

was prepared by adding 1.8 g of Bisphenol A in 9.5 ml of methanol to approximately 900 ml of 6.25 N NaOH. The same procedure was used to prepare saturated etchant except that 0.45 ml of Dowfax was also added. Etchant saturated with Bisphenol A by the paste method and having Dowfax surfactant was prepared by first grinding the Bisphenol A into a fine powder. The powder was slowly worked into a paste by adding dropwise 6.25 N NaOH with constant stirring. To this 0.45 ml of Dowfax was added and the paste was then diluted to one liter with 6.25 N NaOH. Etchant containing GAF RA600 surfactant was prepared by diluting 0.45 ml of GAF RA600 with 6.25 N NaOH to 1 liter. The etchant containing phenol was prepared by dissolving 0.5 g phenol in 6.25 N NaOH and diluting to 1 liter with 6.25 N NaOH.

B. Experimental Results

The data obtained for six different etchants using mild agitation are shown in Table I. The values of Δh represent the average thickness change for the three points of measurement. The indicated uncertainty is the mean deviation of the three measured points for each elapsed time. As can be seen, the deviations, with the exception of etchant I-d, all fall within the expected limits of ± 0.5 microns. This reflects, to the degree of precision of this experiment, rather uniform etching over the surface of the Lexan sheets.

The data obtained for nine Lexan etching solutions are shown in Table II. The data obtained for four different Makrofol KG etching solutions are found in Table III. The values of Δh represent the average thickness change for

Table I.

BULK ETCH RATE STUDIES ON LEXAN USING MILD AGITATION.

Etchant	Elapsed Time (hrs)	Δh (μm)	Bulk Etch Rate ($\mu\text{m/hr}$)	Average
<u>I-a</u> (Sat'd Bisphenol A-precipitate-Dowfax)	20	6.8 ± 0.5	0.17	0.17 ± 0.01
	44	14.7 ± 0.5	0.16	
	68	22.5 ± 0.5	0.16	
	92	31.1 ± 0.2	0.18	
<u>I-b</u> (Sat'd Bisphenol A-Dowfax)	20	6.0 ± 0.4	0.15	0.16 ± 0.01
	44	13.3 ± 0.2	0.15	
	68	20.9 ± 0.4	0.16	
	92	28.5 ± 0.2	0.16	
<u>I-c</u> (Dowfax-6.25 N NaOH)	21	5.2 ± 0.4	0.12	0.13 ± 0.01
	45	11.7 ± 0.2	0.14	
	69	18.2 ± 0.1	0.14	
<u>I-d</u> (Sat'd Bisphenol A)	20	4.4 ± 0.2	0.11	0.12 ± 0.01
	44	10.1 ± 0.9	0.12	
	68	16.0 ± 0.9	0.12	
	92	21.4 ± 0.8	0.11	
<u>I-e</u> (Sat'd Bisphenol A-precipitate)	20	4.2 ± 0.3	0.10	0.09 ± 0.01
	44	8.9 ± 0.3	0.10	
	68	12.9 ± 0.4	0.08	
	92	17.3 ± 0.3	0.09	
<u>I-f</u> (6.25 N NaOH)	21	3.3 ± 0.4	0.08	0.08 ± 0.01
	45	7.3 ± 0.1	0.08	
	69	10.8 ± 0.2	0.07	

Table II.

BULK ETCH RATE STUDIES ON LEXAN USING RAPID STIRRING.

Etchant	Elapsed Time (hrs)	Δh (μm)	Bulk Etch Rate ($\mu\text{m/hr}$)	Average
<u>II-a</u> 6.25 N NaOH-Sat'd (ppt) Bisphenol A- (methanol)-Dowfax	16.00	5.2 ± 0.4	0.16 ± 0.01	0.18 ± 0.02
	24.00	8.4 ± 0.4	0.20 ± 0.02	
	40.00	14.4 ± 0.4	0.19 ± 0.01	
	48.00	16.9 ± 0.5	0.15 ± 0.02	
	64.25	23.1 ± 0.6	0.19 ± 0.01	
	70.50	25.1 ± 0.6	0.16 ± 0.03	
	92.75	33.0 ± 0.3	0.18 ± 0.01	
	111.50	40.2 ± 0.4	0.19 ± 0.01	
		average deviation	0.02	
<u>II-b</u> 6.25 N NaOH-Sat'd (ppt) Bisphenol A- (methanol)	16.00	3.6 ± 0.2	0.11 ± 0.01	0.18 ± 0.04
	24.00	6.4 ± 0.4	0.17 ± 0.02	
	40.00	11.9 ± 1.0	0.17 ± 0.02	
	48.00	15.3 ± 1.1	0.21 ± 0.04	
	64.25	21.6 ± 2.0	0.19 ± 0.03	
	70.50	24.4 ± 2.3	0.22 ± 0.10	
	92.75	33.0 ± 3.1	0.19 ± 0.03	
	111.50	40.8 ± 3.1	0.21 ± 0.03	
		average deviation	0.04	
<u>II-c</u> 6.25 N NaOH-Sat'd (ppt) Bisphenol A- (paste)-Dowfax	17.00	5.5 ± 0.4	0.16 ± 0.01	0.16 ± 0.01
	24.50	7.6 ± 0.4	0.14 ± 0.01	
	41.00	12.7 ± 0.6	0.15 ± 0.01	
	48.00	14.8 ± 0.4	0.15 ± 0.02	
	67.25	21.7 ± 0.9	0.18 ± 0.02	
	96.50	31.7 ± 0.4	0.17 ± 0.01	
		average deviation	0.01	

(continued)

Table II (continued)

Etchant	Elapsed Time (hrs)	Δh (μm)	Bulk Etch Rate ($\mu\text{m/hr}$)	Average
<u>II-d</u> 6.25 N NaOH-Dowfax	16.00	4.7 ± 0.9	0.15 ± 0.03	0.16 ± 0.02
	24.00	7.9 ± 0.4	0.20 ± 0.05	
	40.00	12.1 ± 0.6	0.13 ± 0.01	
	48.00	14.5 ± 0.9	0.15 ± 0.04	
	64.25	19.2 ± 0.9	0.14 ± 0.01	
	70.50	21.3 ± 1.1	0.16 ± 0.03	
	92.75	28.1 ± 0.8	0.15 ± 0.02	
	111.50	34.7 ± 0.9	0.18 ± 0.02	
		average deviation	0.03	
<u>II-e</u> 6.25 N NaOH-0.05% phenol	17.00	4.4 ± 2.5	0.13 ± 0.07	0.16 ± 0.02
	24.50	6.3 ± 3.0	0.13 ± 0.05	
	41.00	11.9 ± 4.5	0.17 ± 0.05	
	48.00	14.2 ± 4.6	0.16 ± 0.03	
	67.50	21.0 ± 6.5	0.17 ± 0.05	
	96.50	30.7 ± 7.9	0.17 ± 0.03	
		average deviation	0.05	
<u>II-f</u> 6.25 N NaOH	16.00	3.7 ± 0.3	0.12 ± 0.01	0.15 ± 0.02
	24.00	6.2 ± 1.1	0.16 ± 0.06	
	40.00	10.8 ± 0.8	0.14 ± 0.01	
	48.00	13.2 ± 1.0	0.15 ± 0.03	
	64.25	17.7 ± 0.8	0.14 ± 0.02	
	70.50	19.7 ± 0.8	0.16 ± 0.07	
	93.00	27.3 ± 1.3	0.17 ± 0.01	
	111.75	33.8 ± 1.3	0.18 ± 0.02	
		average deviation	0.03	

(continued)

Table II (continued)

Etchant	Elapsed Time (hrs)	Δh (μm)	Bulk Etch Rate ($\mu\text{m/hr}$)	Average
<u>II-g</u> 6.25 N NaOH-10 ml methanol	17.00	3.6 ± 0.6	0.11 ± 0.02	0.13 ± 0.02
	24.50	5.2 ± 0.6	0.10 ± 0.02	
	41.00	9.8 ± 0.9	0.14 ± 0.02	
	48.00	11.4 ± 1.0	0.11 ± 0.03	
	67.25	17.2 ± 1.5	0.15 ± 0.02	
	96.50	25.8 ± 2.5	0.15 ± 0.02	
			average deviation	
<u>II-h</u> 6.25 N NaOH-4.5 ml methanol	16.00	3.1 ± 0.3	0.10 ± 0.01	0.12 ± 0.02
	24.00	5.1 ± 0.3	0.12 ± 0.01	
	40.00	9.0 ± 0.3	0.12 ± 0.01	
	48.00	10.6 ± 0.4	0.10 ± 0.02	
	64.25	14.8 ± 0.8	0.13 ± 0.02	
	70.50	16.5 ± 1.0	0.13 ± 0.03	
	93.00	21.6 ± 1.7	0.11 ± 0.02	
	111.75	27.2 ± 2.3	0.15 ± 0.02	
		average deviation	0.02	
<u>II-i</u> 6.25 N NaOH-GAF RA600	17.00	3.0 ± 0.2	0.09 ± 0.01	0.10 ± 0.02
	24.50	4.4 ± 0.4	0.09 ± 0.02	
	41.00	8.3 ± 0.3	0.12 ± 0.01	
	48.00	9.4 ± 0.2	0.08 ± 0.01	
	67.25	14.50 ± 0.5	0.13 ± 0.01	
			average deviation	

Table III.

BULK ETCH RATE STUDIES ON MAKROFOL KG USING RAPID STIRRING

Etchant	Elapsed Time (hrs)	Δh (μm)	Bulk Etch Rate ($\mu\text{m/hr}$)	Average
<u>III-a</u> 6.25 N NaOH	3.00	0.4 ± 0.3	0.07 ± 0.05	0.10 ± 0.04
	7.00	1.1 ± 0.3	0.08 ± 0.03	
	11.25	2.4 ± 0.4	0.16 ± 0.03	
	26.50	5.4 ± 0.4	0.10 ± 0.01	
	average deviation			
<u>III-b</u> 6.25 N NaOH-Sat'd (ppt) Bisphenol A- (paste)	3.00	0.6 ± 0.3	0.10 ± 0.04	0.13 ± 0.02
	7.00	1.6 ± 0.4	0.13 ± 0.02	
	11.25	2.9 ± 0.3	0.15 ± 0.01	
	26.50	7.1 ± 0.5	0.14 ± 0.01	
	average deviation			
<u>III-c</u> 6.25 N NaOH-Sat'd (ppt) Bisphenol A- (paste)-Dowfax	3.00	$-0.1 \pm 0.1^*$	$-0.00 \pm 0.02^*$	0.15 ± 0.03
	7.00	1.1 ± 0.2	0.14 ± 0.02	
	11.25	2.7 ± 0.2	0.18 ± 0.02	
	26.50	6.6 ± 0.3	0.13 ± 0.04	
	average deviation			
<u>III-d</u> 6.25 N NaOH-Dowfax	3.00	$-0.08 \pm 0.2^*$	$-0.01 \pm 0.03^*$	0.16 ± 0.06
	7.00	0.9 ± 0.3	0.12 ± 0.04	
	11.25	2.9 ± 0.2	0.23 ± 0.03	
	26.50	6.5 ± 0.2	0.12 ± 0.01	
	average deviation			

*See explanation in discussion.

three distinct points on each of three pieces of plastic--making a total of nine points of measurement. (Exception is solution II-f, 6.25 N NaOH, which contained only two sheets, and therefore is the result of six points of measurement). The indicated uncertainty for Δh is the standard deviation of the nine (or six) average thickness changes. The value of the bulk etch rate for each individual time period is once again the result of nine (or six) individual etching rates. The uncertainty of each of these values is the standard deviation of the individual etching rates. The average overall bulk etching rate is the average of the average bulk etching rate for the different time intervals with the uncertainty being the standard deviation of these values.

C. Discussion

It is apparent from viewing Table I that the presence of Dowfax 2A1 surfactant leads to an increase in the bulk etch rate. Since the surfactant allows for more intimate contact between the solution and the surface of the plastic, this is not unexpected. The most probable role of the surfactant here is the reduction of surface tension at the etchant-Lexan surface.

Paretzke^[8] and Peterson^[1] both noted a sudden jump in the etch rate when the solution became saturated with the etch products of Lexan. Paretzke has suggested that the etch product particles may adsorb on their surface, surfactant molecules previously bound on the surface of the plastic. Thus more surface of the plastic would be exposed to attack and the rate would increase. The results for etchants I-a and I-b in these experiments, however, do not

differ significantly as would be expected if Paretzke's idea were correct.

Another possible explanation is that Bisphenol A may itself be acting as a surfactant. Surfactant molecules with molecular weights as low as 200 are known (molecular weight of Bisphenol A is 228) and surfactant solutes usually display maximum surface activity and functional effectiveness when they are near the threshold of insolubility.^[9] Bisphenol A may be acting independently or in a synergistic way with the Dowfax surfactant. It is interesting that the rate enhancement due to Dowfax 2A1 and Bisphenol A is nearly additive. Under the conditions of these experiments, the enhancement due to Dowfax is 0.05 $\mu\text{m/hr}$ whereas the enhancement due to Bisphenol A averages to 0.02. Etchants I-a and I-b show a net enhancement of about 0.08.

The results for etchants I-d and I-e do not seem consistent. It should be noted, however, that the deviations obtained for etchant I-d are considerably larger than the other etchants indicating a very nonuniform etch. This may have been due to the nature of the particular piece of Lexan used. Further study would be needed to clarify this.

In comparing the results for Lexan under the different conditions of agitation several things become apparent. Etchants II-b, II-d and II-f (Table II) all show a considerably larger etch rate when the agitation is more vigorous. However, etchants II-a and II-c do not exhibit this effect. The greatest percentage change is noted for those solutions not containing the Dowfax surfactant. Comparing the deviations of etch rates for a given etchant in Table II indicates that the smoothest etch is obtained with etchants II-a and II-c followed by II-d and then by II-f and II-b, respectively. The best surfactant seems to be a combination of Dowfax with saturated Bisphenol A.

The results of these experiments suggest that the more effective the surfactant (in terms of uniform etch) the less influence has the stirring rate on the etch rate. This is reasonable if one considers what goes on at the etchant-Lexan interface. With an etchant such as aqueous sodium hydroxide, the surface tension is relatively large resulting in restricted contact between the phases. Agitation of the solution, as by stirring, can mechanically increase the amount of contact and thus the etching rate. With an effective surfactant in the solution, the amount of contact between the two phases is already extensive and increasing the stirring rate does not have as large an effect on the amount of contact and, thus, the etch rate.

One can also deduce from these results that the more effective the surfactant the less influence increased stirring rate has on the uniformity of the etch. Etchants without good surfactants present show, on the other hand, a large dependence on stirring rate. Both the etch rate and the nonuniformity of the etch increase with increasing stirring rate for the latter.

The results for Bisphenol A in the absence of Dowfax 2A1 do not indicate surfactant behavior for this molecule taken by itself. It does exhibit, however, a definite rate enhancing effect. The rate controlling step for basic ester hydrolysis is a nucleophilic attack at the carbonyl carbon.^[10] Either OH⁻ or the bisphenolate ion could behave as the nucleophile. Bisphenolate may be more effective as its organic nature should make it more compatible with the polycarbonate. This question merits further study.

Since methanol was used as one means to prepare solutions saturated in Bisphenol A, the effect of methanol alone on the etching process was studied.

These results (II-g and II-h) show that the presence of methanol decreases the etch rate somewhat. The reason for this is unclear at the moment. One of the major organic components of the etch products is phenol so etchant II-e was prepared. The etch rate compared to aqueous sodium hydroxide is not significantly changed but the uniformity of the etch is severely affected. The etchant with phenol present gave the most irregular etch of all the etchants studied. The phenolate ion, like the bisphenolate ion, may behave as a nucleophile in the hydrolysis of the polycarbonate. Its organic nature as well as its smaller size may allow it to penetrate further into the solid and thus yield a less uniform etch.

In view of the large importance of the surfactant in controlling the nature of the etch, it is felt that the study of surfactants other than Dowfax 2A1 could be quite profitable. The surfactant included in these studies was GAFAC RA-600.^[11] This formulation was chosen because of its extensive alkali solubility and alkali stability. The results (etchant II-i, Table II) show a considerable depression of the etch rate, but the etch was so even that the plastic remained quite clear. This is a definite advantage in terms of optical studies. Unfortunately, however, this surfactant enhances the etch rate at strained points in Lexan. This occurs to such an extent that it is difficult to keep the plastic suspended in the etch solution as it etches very rapidly at the point of suspension. In view of the earlier discussion, it would be interesting to study the influence of stirring on the behavior of this etchant.

Makrofol KG

Due to the fact that Makrofol KG is so thin, the experiments lasted at most about one day before the plastic was etched off the hangers. From these initial results, it is felt that the bulk etch rate of Makrofol KG may not be independent of etch products as put forth by Paretzke.^[8] As seen from Table III, there is indeed a difference in thickness change between the solution of 6.25 N NaOH and the other three solutions. As might be noted the accuracy of these measurements are well within the limits of the apparatus used.

There seems to be an initial hinderance of the plastic to etch. There are indeed two possible explanations for this: the plastic swells in solutions or the initial surface of the plastic slows etching. Both Makrofol KG and Lexan were put into water and water with Dowfax for 63 hours. At the end of that time, there was no noticeable change in thickness. Therefore, if a swelling occurs, it is not something as simple as the plastic absorbing water. In highly concentrated solutions, like the 6.25 N NaOH solution, charged ions may migrate into the plastic causing water to diffuse into the plastic by osmosis. This theory has yet to be tested.

Note: Makrofol KG has the same chemical composition as Lexan (Grade 8070-112) except that it contains a small amount of a green dye. The two differ, however, in that Lexan is an extruded product while Makrofol KG is prepared by a casting process.^[12] The degree of crystallinity and other structural features may be quite different for the two plastics.

II. AUTOMATED TECHNIQUES FOR PARTICLE TRACK ANALYSIS

In order to speed up the process of track data acquisition and analysis, a study was carried out to determine the feasibility of using the various previously developed techniques. It was found that an automated microscope, together with a digital TV type system represents the most promising approach in this area. Specifically, it was found that a system such as the Quantimet 720 can be used to count and measure various track parameters such as area, perimeter, horizontal and vertical projections, etc. It was judged that the flexibility of the system would be considerably enhanced if it were also interfaced with a mini-computer. This would allow the recording of the coordinates of each track as well as aid in pattern recognition.

III. PARTICLE IDENTIFICATION USING AgCl CRYSTALS

A set of exposures were performed of AgCl crystal detectors to 7 MeV alpha particles, fission fragments, 160 MeV/nucleon-¹⁶O, 1.05 GeV/nucleon-¹⁶O, and 2.1 GeV/nucleon ¹²C and ¹⁶O particles. Measurements of track opacity revealed that charge separation is possible with the AgCl crystals. However, since these detectors are not sensitive to the higher energy δ -rays, the charge resolution is not as good as that with nuclear emulsions.

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