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## The Effects of Cationically Charged Titanium Dioxide on Particle Dispersion in the Sheet of Paper

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THE EFFECTS OF CATIONICALLY  
CHARGED TITANIUM DIOXIDE ON  
PARTICLE DISPERSION IN THE  
SHEET OF PAPER

Submitted to Dr. Stephen  
Kukolich in fulfillment  
Senior Thesis course 471.

Neil A. Hartman  
Winter term of 1969

## ABSTRACT

Comercial bleached soft wood sulfite pulp was used. The pulp was refined in a Standard Valley Beater to a Canadian Standard freeness of 428. This pulp was preserved and used to make all of the handsheets, on a Noble and Wood handsheet mold.

The Titanium dioxide added to the handsheets was prepared in three different ways: simple dispersion, dispersion of the Titanium dioxide along with cationic substances, and addition of the dispersed Titanium dioxide and the cationic substance to the pulp without previous co-dispersion. The optical properties of the sheets were measured and the Titanium dioxide in the sheets was found by an ash analysis. The scattering coefficient of the Titanium dioxide in the sheets was then determined with the Judd chart of the Kubelka-Munk equation. The percents of retention were also determined.

The results also indicate that there are optimum percent levels of cationic polyamide (PA) based on the weight of the Titanium dioxide. At one percent level the method of co-dispersion can produce a three dollar per ton of five percent Titanium dioxide paper, savings. The savings over using un-treated Titanium dioxide is about six dollars per ton on a run of paper which was five percent un-treated Titanium dioxide.

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## LITERATURE SURVEY

Titanium dioxide is refined from ilmenite ore, rutile ore, and Titanium dioxide slags. The end product is crystallized into one of two forms, rutile or anatase. Rutile titanium dioxide has a refractive index of 2.75, specific gravity of 4.2, brightness between 97 and 99, and a cost of 27¢ per pound. Anatase Titanium dioxide has a refractive index of 2.55, specific gravity of 3.9, brightness between 96 and 98, and a cost of 25¢ per pound. The best average particle size for use in the paper industry is 0.3 microns.(10)

The refractive index of either form is considerably higher than ~~any other~~ the refractive index of any other pigment used in the paper industry. Because of this Titanium dioxide is used to impart opacity to types of paper which cannot be satisfactorily produced with other types of pigments. A few such paper types are air mail paper, light weight printing paper (an example is Bible paper), and opaque waxed paper.(10)

In 1960 the paper industry consumed 45,000 tons of Titanium dioxide as a wet end additive. This represents an expenditure of around \$23,000,000. Therefore, any method of increasing the efficiency of Titanium dioxide will be appreciated by the paper industry.(10)

In this experiment the effectiveness of the Titanium dioxide will be determined by a handsheet analysis. In order to do this the brightness, opacity, basis weight, sheet moisture, ash composition must be *calculated*. These values are then analyzed by the Judd chart of the Kubelka-Munk equation. The results can be used to compare the opacifying power of the Titanium dioxide in the various sheets. as well as the percent retention of the Titanium dioxide. (A sample calculation and a couple of comparative graphs are on pages I and II of the appendix)

There are a host of variables involved in making a handsheet analysis. (10) When one is dealing with optical properties one of the most important variables is pressing. By increasing the pressure on the wet handsheet the fibres and pigment particles are brought into closer proximity. This enables the surface tension of the drying water to bring the fibers and particles close enough together that they bond. This increase in bonding reduces the area of reflecting and refracting surface thus reducing the scattering coefficients of the fibre and pigment.

A primary determinant of retention is the electrokinetic-potential between the pulp fibers and the Titanium dioxide particles. (16) The magnitude of this electrokinetic-potential is strongly dependent on the pH. Also, there must exist a pH level for maximum retention. This optimum pH is usually between pH 5 and pH 6 for Titanium dioxide. (12)

Suspensions of cationically charged Titanium dioxide particles have been prepared by mixing Titanium dioxide with  $\text{AlCl}_3$ . These suspensions did not settle or flocculate over periods of several months. Unfortunately, this particular type of dispersion is worthless because Titanium dioxide particles thus treated have a lower retention level than untreated Titanium dioxide.(15) The above experiment sheds a dim light on the primary hypothesis of this paper. However, many other cationic reagents are useful in increasing the retention of Titanium dioxide. (2,5,17) One of the most promising types of retention aids is cationic polymers of which the polyamide used in this experiment is an example.(17)

The retention of cationic materials is dependent on charge molecular weight(the molecular weight of the material divided by the number of charge equivalents per mole). A higher charge molecular weight will correspond with a higher weight percent of retention. (5) It is possible that the pulp fibers can only adsorb a certain amount of cationic material before they also become cationic and therefore electrostatically repulsive to additional cationic material. Additional retention beyond this point would be due to mechanical entrapment. If the above reasoning is correct than the retardation of Titanium dioxide by treating it with  $\text{AlCl}_3$  would be due to the very low charge equivalent weight of the  $\text{Al}^{+++}$  ion. A very small amount of  $\text{Al}^{+++}$  could change the surface charge of the fibres causing them to repel additional cationic Titanium dioxide particles.

Cationic materials are used commercially as retention aids by adding them directly to the furnish with pulp and Titanium dioxide already in it. Co-dispersing the Titanium dioxide along with cationic materials, in order to make the particles cationic will be of little or no commercial value unless it aids retention and/or increases the opacifying power of the Titanium dioxide particles more so than the direct addition of the cationic material to the furnish.



## EXPERIMENTAL DESIGN

The primary hypothesis is that dispersing the Titanium dioxide along with cationic substances will cause the surfaces of the Titanium dioxide particles to become cationically charged. This should cause the particles to become mutually repulsive and therefore discrete ( resistant to flocculation ). Wood pulp fibers develop an anionic surface charge when they are dispersed in water, because of this an attractive electrokinetic-potential should exist between the the pulp fibers and the cationically charged Titanium dioxide particles. This electrokinetic-potential should aid retention of the Titanium dioxide particles as long as it is attractive. After the fibers are neturalized electrically by absorption of cationic particles any additional retention would be due to mechanical entrapment. If the mechanically entrapped particles are also cationic then this would cause the fibers to become cationic, thus retarding additional retention by electrokinetic repulsion.

This hypothesis is tested by measuring the percent of retention and plotting it against the percent level of addition of the Titanium dioxide. The relative heights of the curves indicate the retention efficiency. The retention efficiency is assumed to be strongly influenced by the electrokinetic-potential. The scattering coefficient of the Titanium dioxide in the sheets is calculated using the Judd chart of the Kubelka-Munk equation. The scattering coefficient

is plotted against the percent of Titanium dioxide in the sheet. The relative heights of the curves thus obtained indicate the degree of dispersion of the Titanium dioxide particles. Increased dispersion would create a larger surface area for the reflection and refraction of light. This would cause the scattering coefficient of the Titanium dioxide to be higher. Therefore, the same opacity could be imparted to a sheet of paper with less Titanium dioxide. (Graphical examples of these concepts are on page II of the appendix)

A commercial bleached soft wood sulfite pulp was used. The pulp was refined in a Standard Valley Beater in accordance with TAPPI test standard T-200 m-58, to a freeness of 428 (TAPPI test standard T-227 ts-61). This pulp was preserved and used to make all of the handsheets on a Noble and Wood handsheet mold (TAPPI test standard T-205 m-58).

The sheets were filled with Titanium dioxide which was dispersed in a malted milk mixer at the percent solids given on pages III, V, and VII of the appendix. There was no point in controlling the pH because it always fell in the narrow range of pH 6.8 to pH 7.1.

The sheets were conditioned (TAPPI T-404 m-49) and weighed. They were then analyzed for brightness (TAPPI T-402 m-49) and opacity (TAPPI T-452 m-52); also SX, S  $\text{TiO}_2$ , S fibre, %  $\text{TiO}_2$ , % retention, % addition, and basis weight in accordance with page I of the appendix.

## DISCUSSION OF RESULTS

Page III of the appendix shows that decreasing the percent of PA based on the weight of the Titanium dioxide over the range 5.29 percent to 1.49 percent increases the value for  $S\ TiO_2$ . This suggests that a further decrease in the percent of PA would increase the the value for the  $S\ TiO_2$  even more. It should also be noted that the  $S\ TiO_2$  value for the 1.49 percent PA that was not co-dispersed is well below the curve for the 1.49 percent PA that was co-dispersed.

The retention of the  $TiO_2$  which was treated with 1.49 percent PA by co-dispersion is highest (pageIV), however, the retention of the  $TiO_2$  treated with 1.49 percent PA without co-dispersion is only slightly lower.

When preparing the  $TiO_2$  for group II of the PA it was noted that the usage of one percent or less of PA at 50 percent solids turned the solution into a gel which would not flow. A slight increase of the percent level above the one percent level turned the dispersion back into a low viscosity liquid. Because of this the  $TiO_2$  and the PA were co-dispersed at the indicated lower percent of solids.(page V of the appendix).

The plot of group II on page V of the appendix shows that decreasing the percent level of PA from 1.24 to .740 causes the value for the  $S\ TiO_2$  to decrease and a further

decrease in the percent of PA from .740 to .462 and .100 increased the value for the S  $\text{TiO}_2$ . Page VI of the appendix shows that 1.24 percent of PA gives the best retention of the four percent levels.

Group III (pages VII and VIII of the appendix) compares the efficiency of  $\text{TiO}_2$  co-dispersed with 1.30 percent of PA with the efficiency of  $\text{TiO}_2$  with 1.30 percent PA without co-dispersing them. The  $\text{TiO}_2$  which was co-dispersed gave a higher S value for the  $\text{TiO}_2$ , indicating that the dispersion on the fibers was better. However, the  $\text{TiO}_2$  that was not co-dispersed had better retention properties.

## CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

The most significant conclusions are directly related to the economic analysis on pages IX - XI of the appendix. By creating a better dispersion of the Titanium dioxide on the fibres one can obtain the same SX value for the sheet with less Titanium dioxide. This means a savings of three dollars and fifty cents per ton of paper which is five percent Titanium dioxide, by co-dispersing the Titanium dioxide with 1.30 percent PA over addition of 1.30 percent PA to a furnish which already contains the the Titanium dioxide. A similar cost comparison applied to group one of the polyamide shows that six dollars per ton can be saved on the cost of producing a sheet with five percent un-treated Titanium dioxide by co-dispersing the Titanium dioxide along with 1.49 percent PA.

When paper is made to the same SX value with a lower percent of well dispersed Titanium dioxide it will have different physical and optical properties. Some predicted changes caused by this follow: lower sheet density, higher burst because of less interference with fibre to fibre bonding, a lower brightness and a higher opacity.

Further work needs to be done in this area of study. The effects of pH on cationically treated Titanium dioxide particles needs to be examined. Special interest should be devoted to examining the pH ranges 5-6 and 8-9, the higher

pH range corresponds with that used for aquapel sizing. The effects of time on the efficiency of Titanium dioxide treated by co-dispersing along with cationic polyamide should also be examined. This would determine how closely the Titanium dioxide thus treated must be added to the headbox for optimum dispersion.

## APPENDIX

# SAMPLE CALCULATION

## Titanium dioxide slurry

200g Titanium dioxide

200g water

5.96g PA 50% active

50%  $TiO_2$  approximately

1.49% PA =  $PA/TiO_2$

## Pulp

8"x 8" handsheets 4% moisture

Sheet weight = 3.066g

Brightness = 84.2

Opacity = 79.8

Basis weight = 45.7 lbs./24x36x500 ream

Ash weight = .0131g

SX = 2.45

S =  $2.45/45.7 = .0537$

## Titanium dioxide filled handsheet

8"x 8" handsheet 4% moisture

Sheet weight = 2.682g

Brightness = 89.0

Opacity = 88.1

Basis weight = 38.4 lbs./24x36x500 ream

Ash weight = .1339g

$TiO_2$  weight = .1229 =  $.1339 - (.0131) \times (2.682/3.066)$

%  $TiO_2$  = 4.40% =  $.1229/(2.682 \times .96)$

SX = 4.12

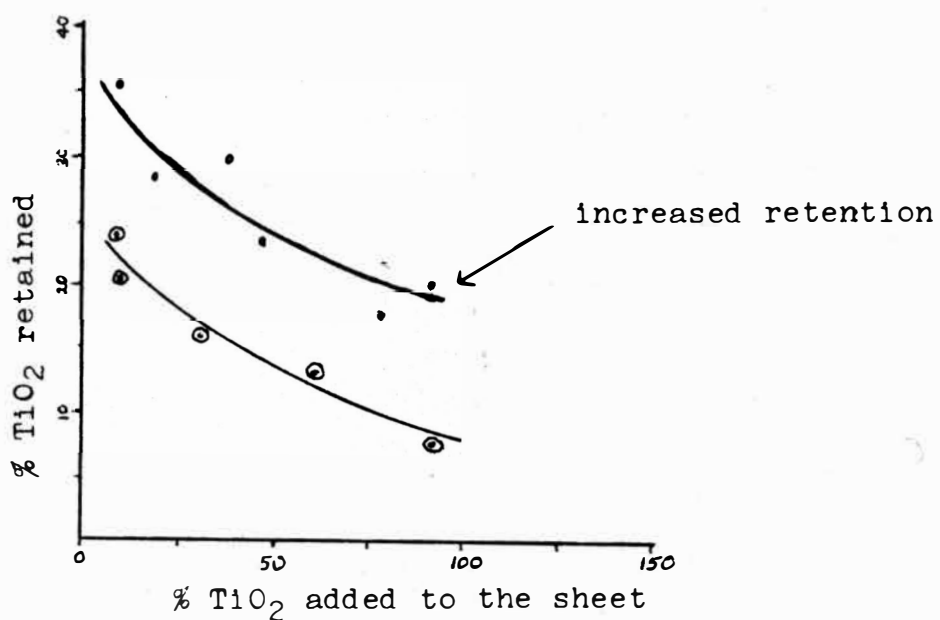
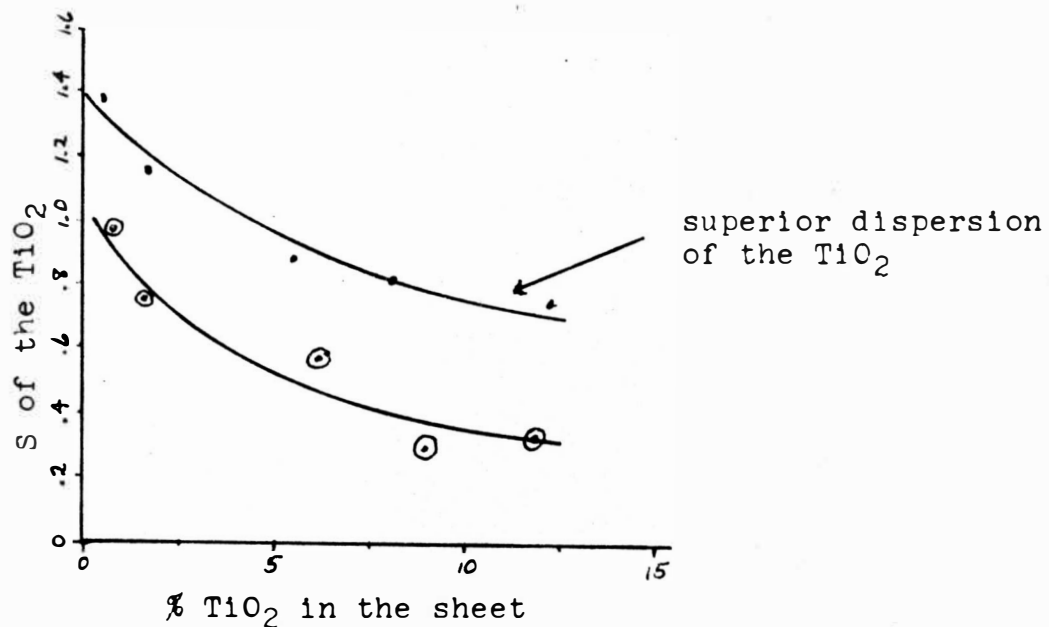
S  $TiO_2$  = 1.27 =  $\frac{4.12/38.4 - .956(.0537)}{.0440}$

% retention = 47.2% =  $.1229/.26g TiO_2$

% addition = 10.7% =  $\frac{.26}{(2.682) \times .96 - .1229}$



GRAPHICAL EXAMPLES OF SX VERSUS PERCENT TITANIUM LIOXIDE  
AND PERCENT RETENTION VERSUS PERCENT OF ADDITION

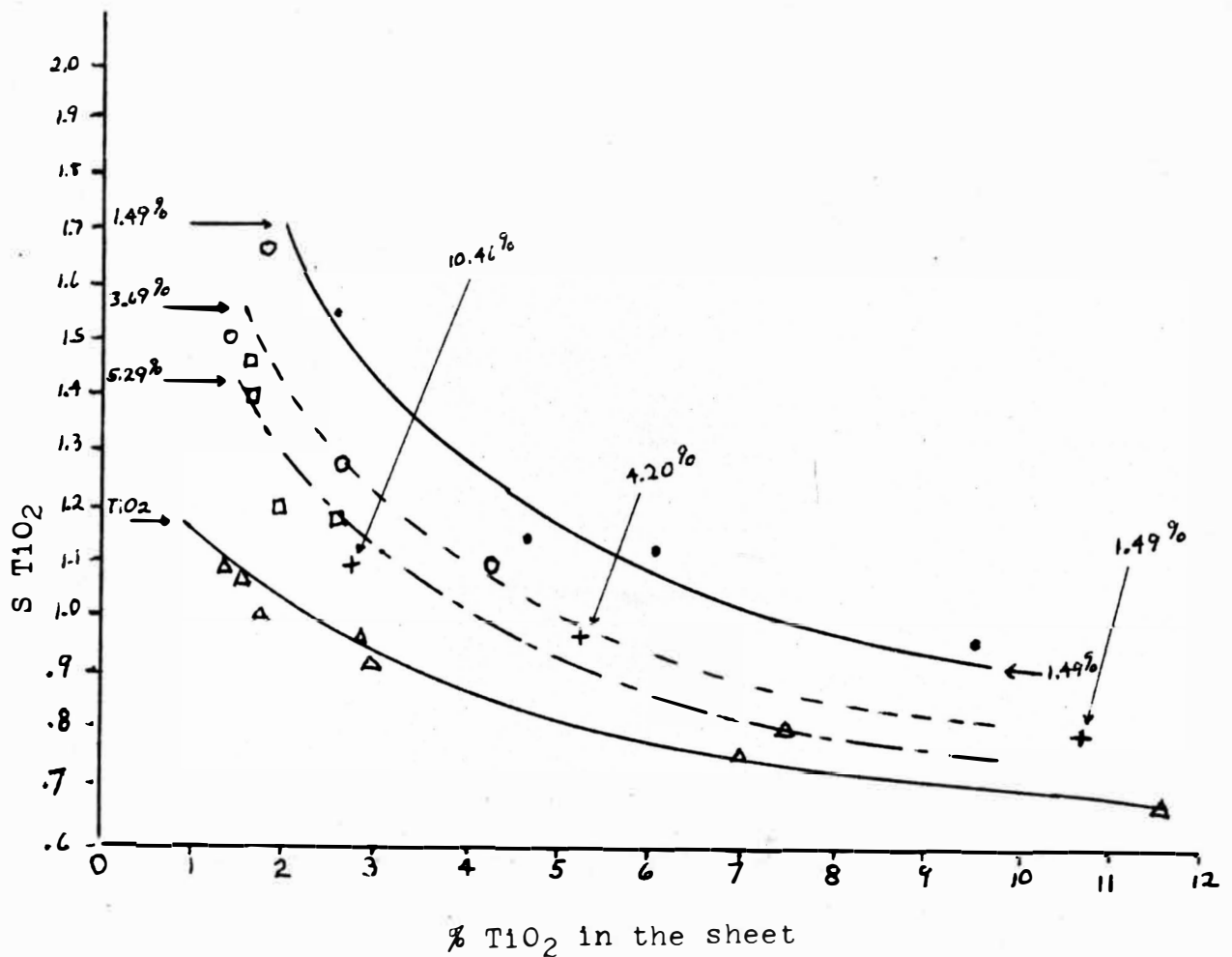


# POLYAMIDE GROUP I

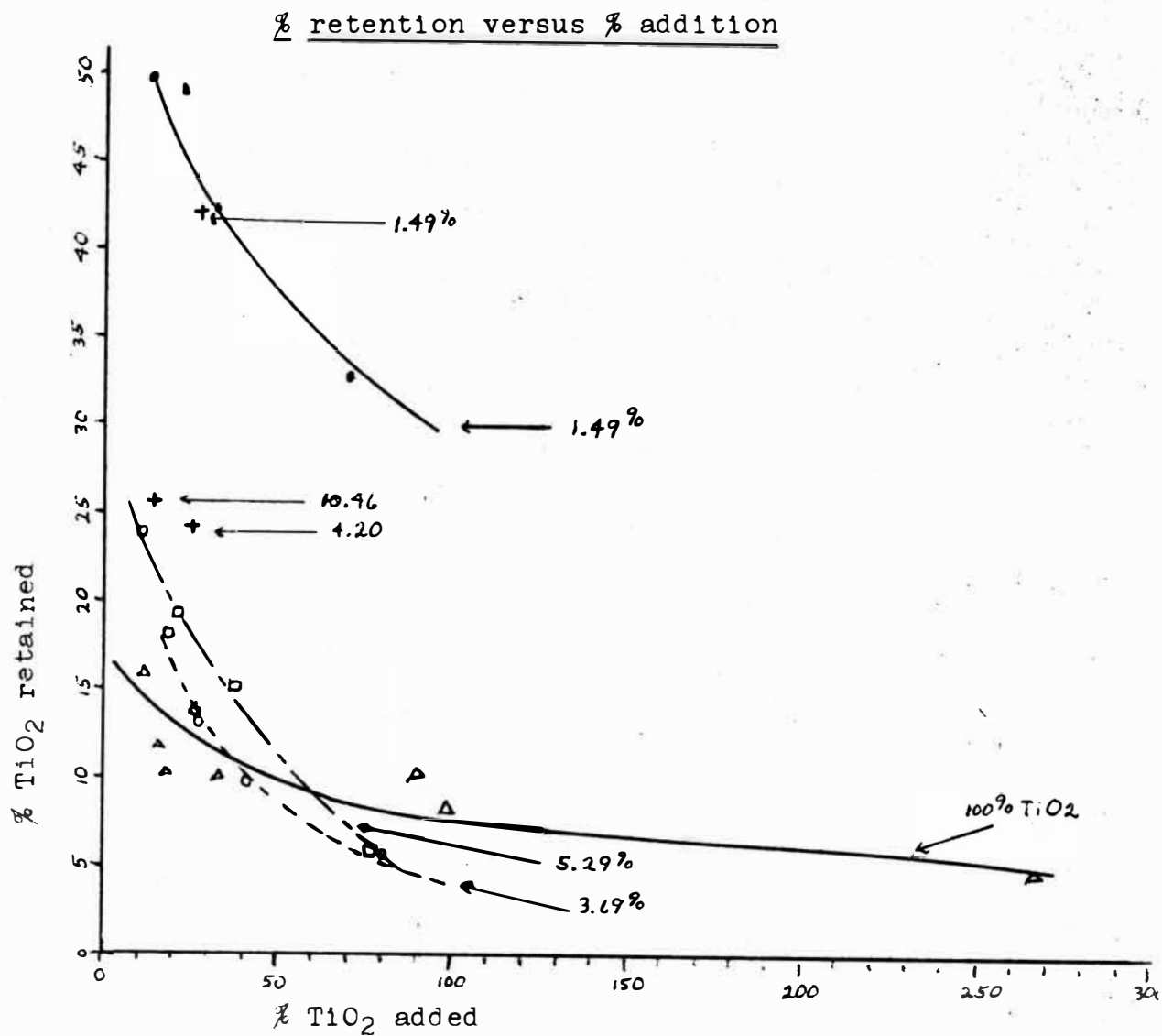
Key to the graphs

- $\text{TiO}_2$  with 1.49% PA co-dispersed at 50% solids
- $\text{TiO}_2$  " 3.69% " " " "
- $\text{TiO}_2$  " 5.29% " " " "
- △  $\text{TiO}_2$  dispersed at 50% solids
- +  $\text{TiO}_2$  with the indicated % PA (not co-dispersed)

S  $\text{TiO}_2$  versus %  $\text{TiO}_2$  in the sheet



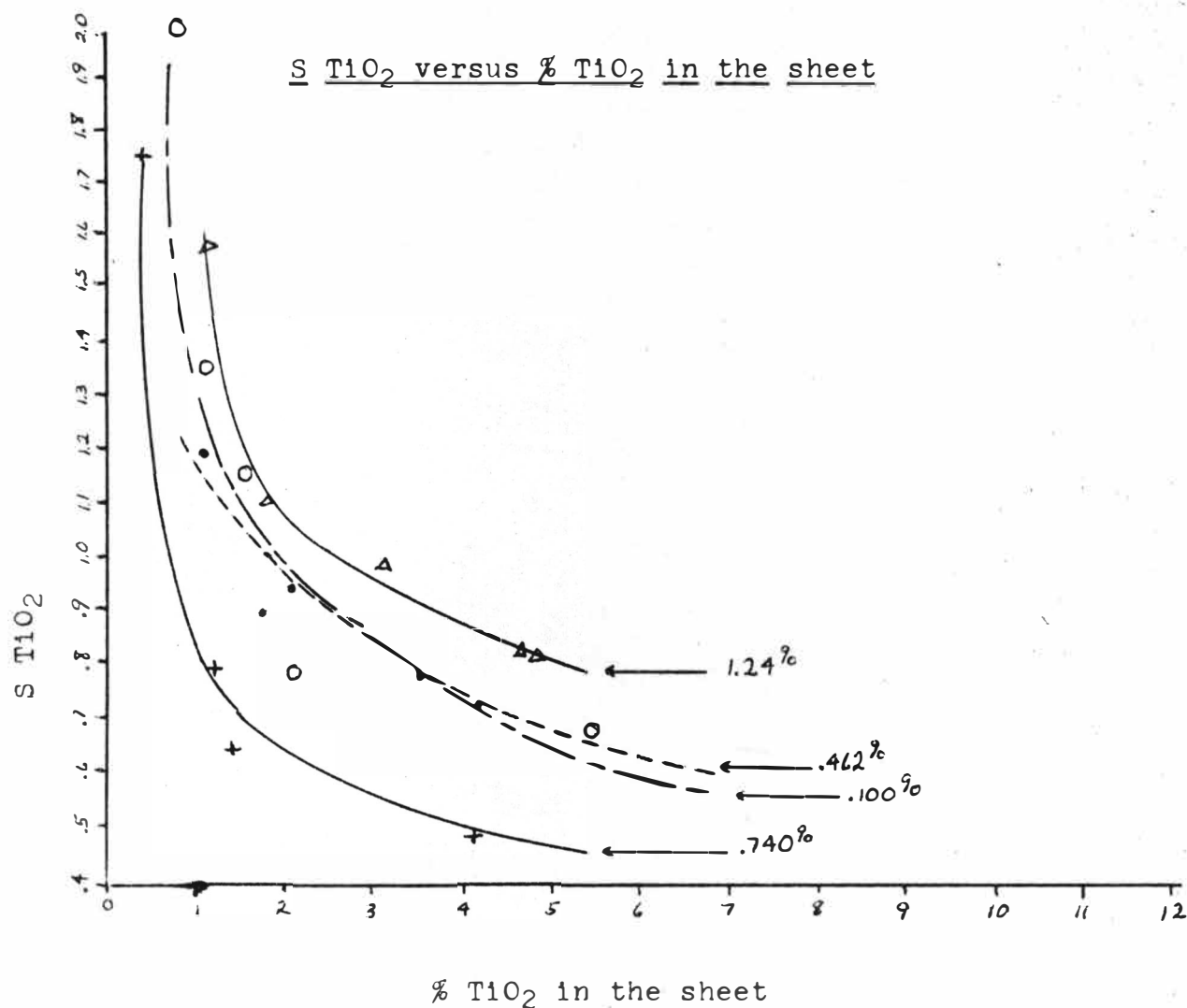
# POLYAMIDE GROUP I (cont)



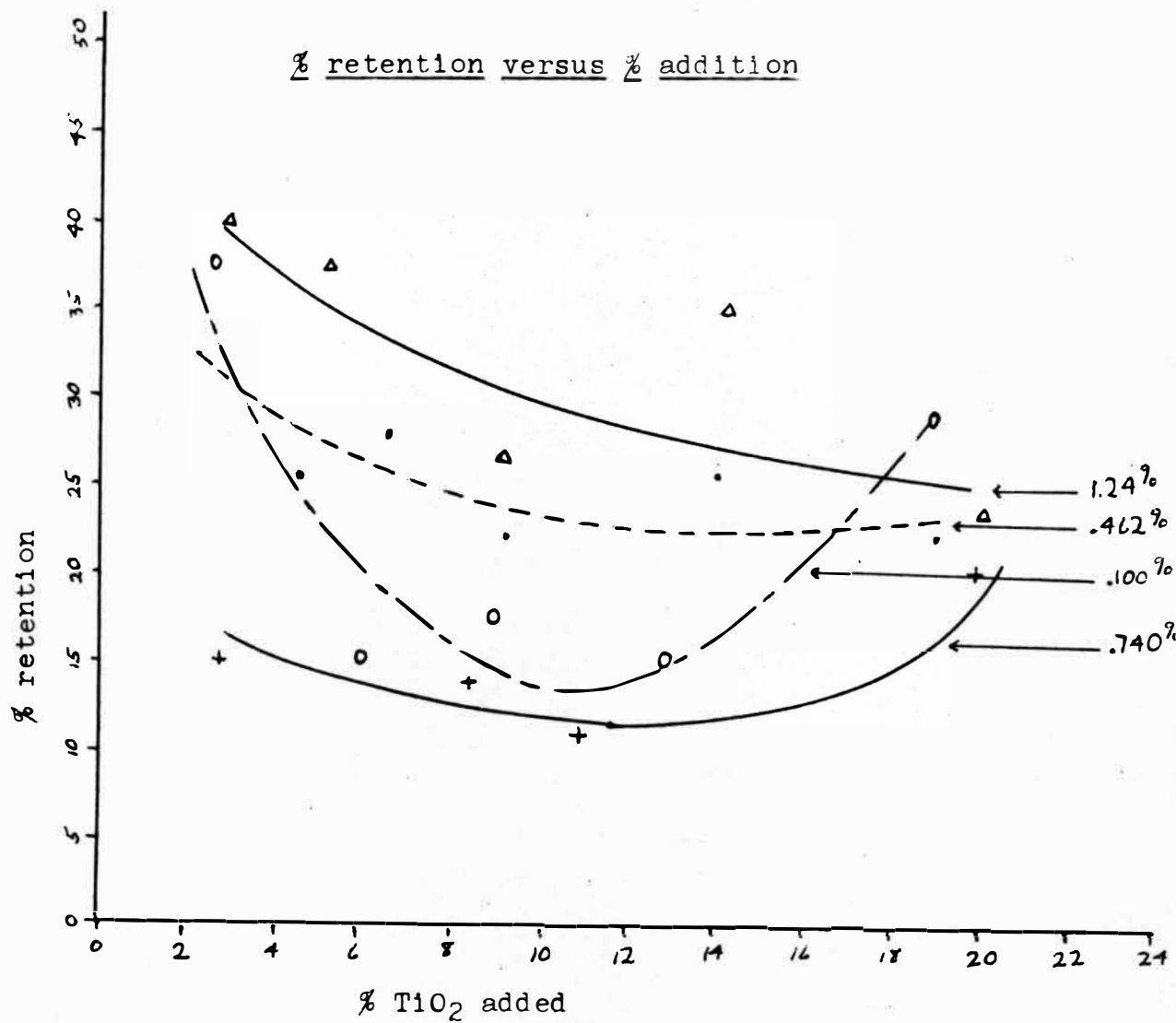
# POLYAMIDE GROUP II

Key to the graphs

—▲—	TiO <sub>2</sub>	with 1.24% PA co-dispersed at 20.8% solids
—○—	TiO <sub>2</sub>	" .100% PA " " 20.8% "
—•—	TiO <sub>2</sub>	" .462% PA " " 24.2% "
—+—	TiO <sub>2</sub>	" .740% PA " " 25.4% "



POLYAMIDE GROUP II (cont)

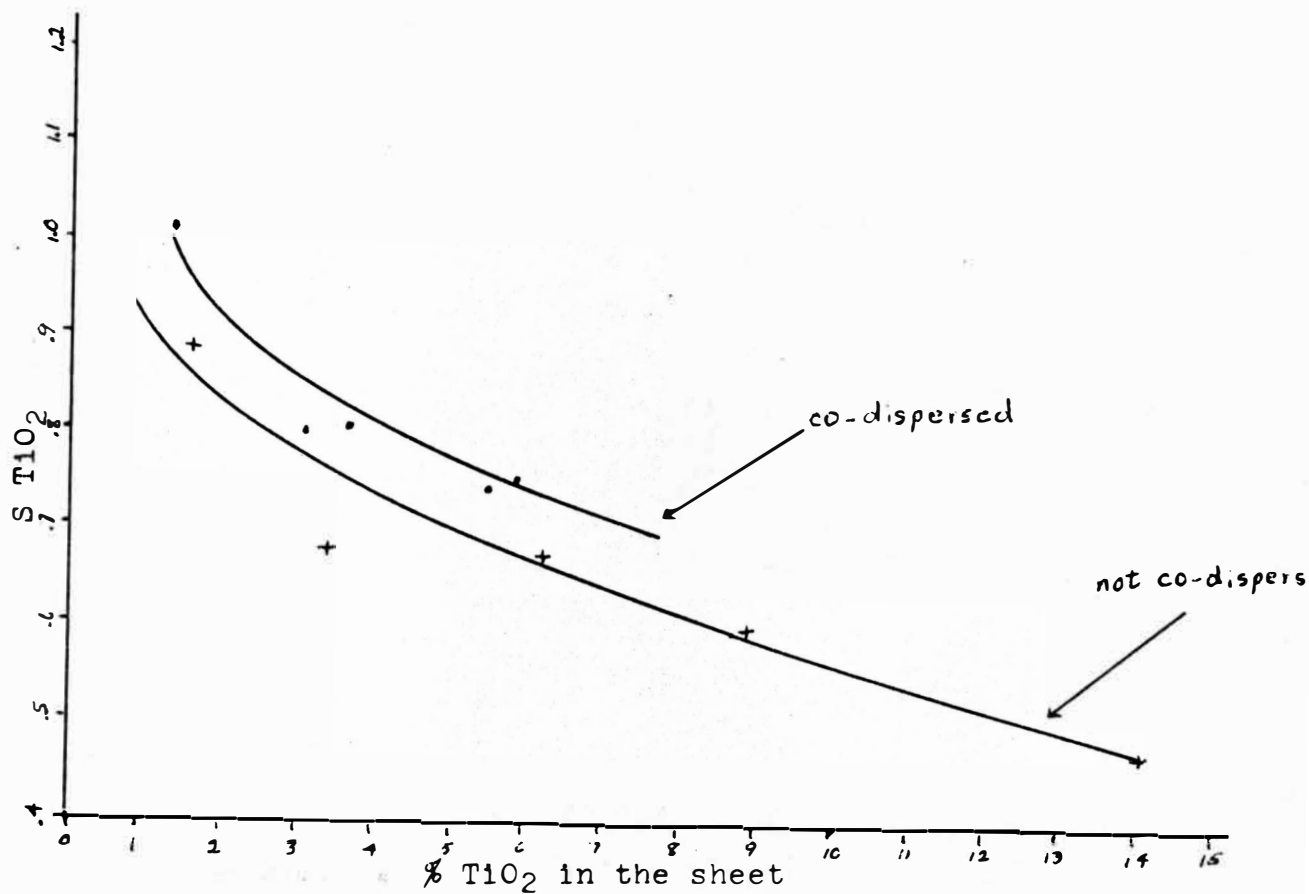


# POLYAMIDE GROUP III

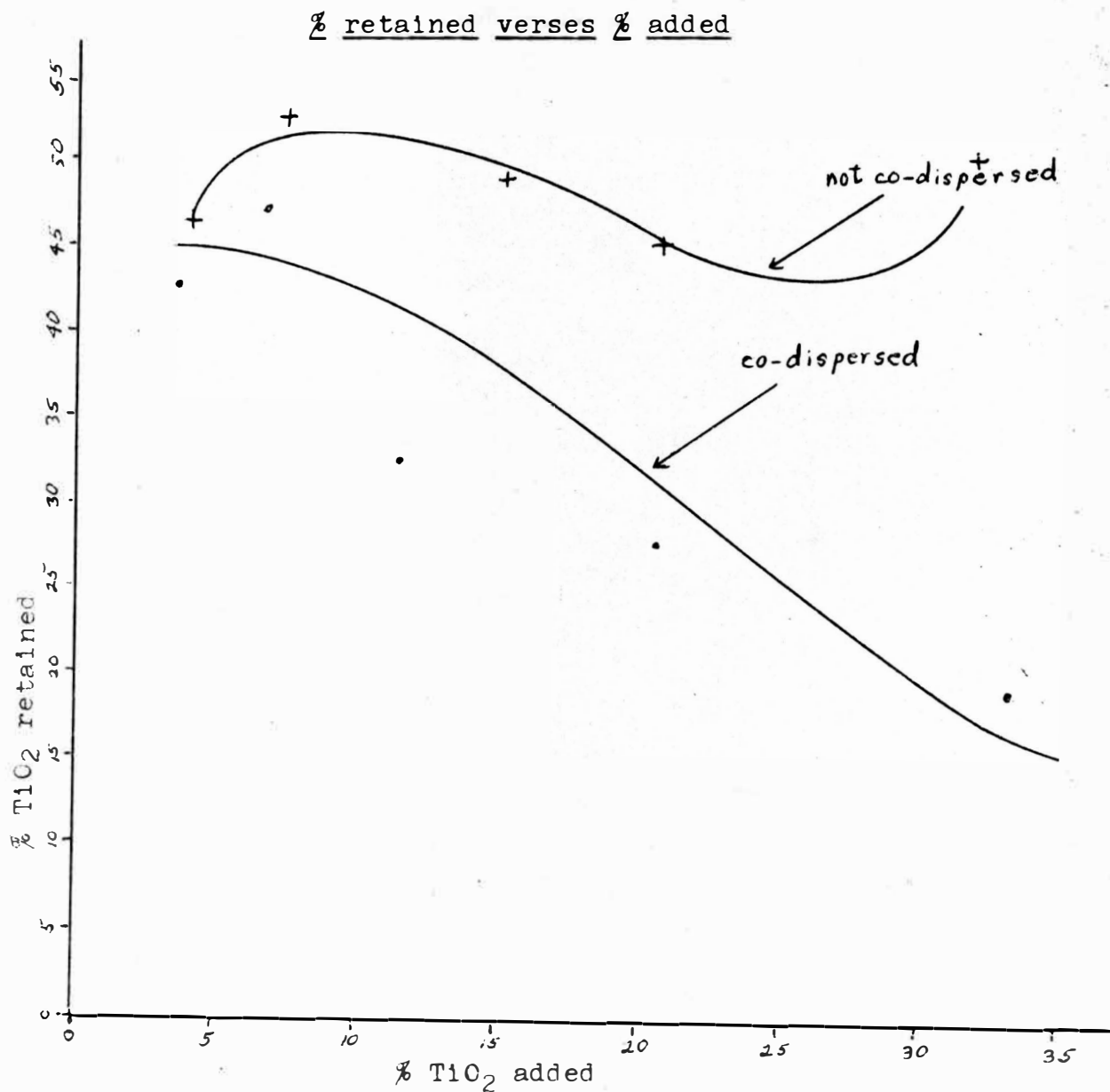
Key to the graphs

- $\text{TiO}_2$  with 1.30% PA co-dispersed at 19.0% solids
- +  $\text{TiO}_2$  dispersed at 20.9% solids plus 1.30% PA (not co-dispersed)

S  $\text{TiO}_2$  versus %  $\text{TiO}_2$  in the sheet

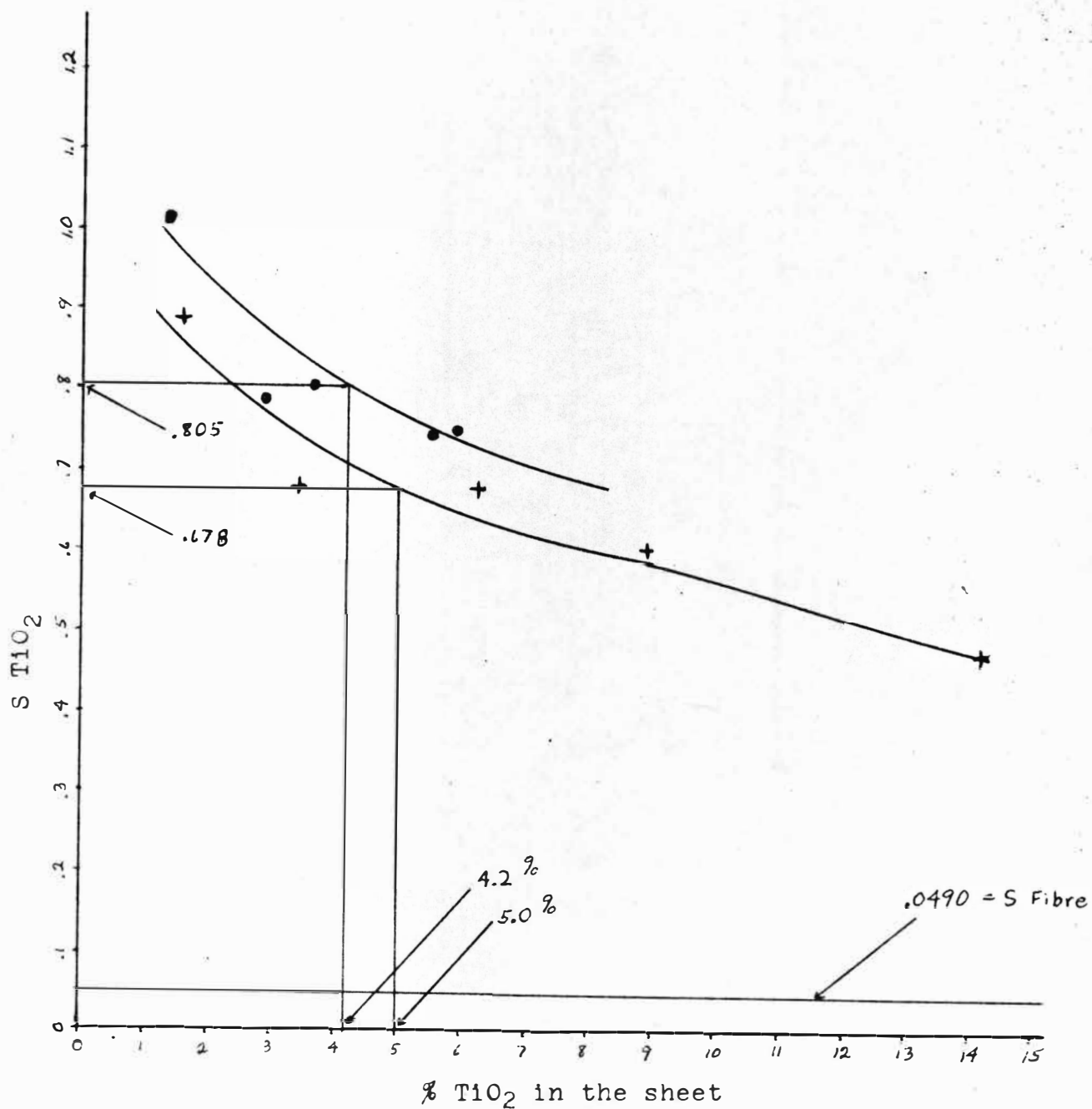


POLYAMIDE GROUP III (cont)



# GRAPHICAL ANALYSIS FOR ECONOMIC ANALYSIS

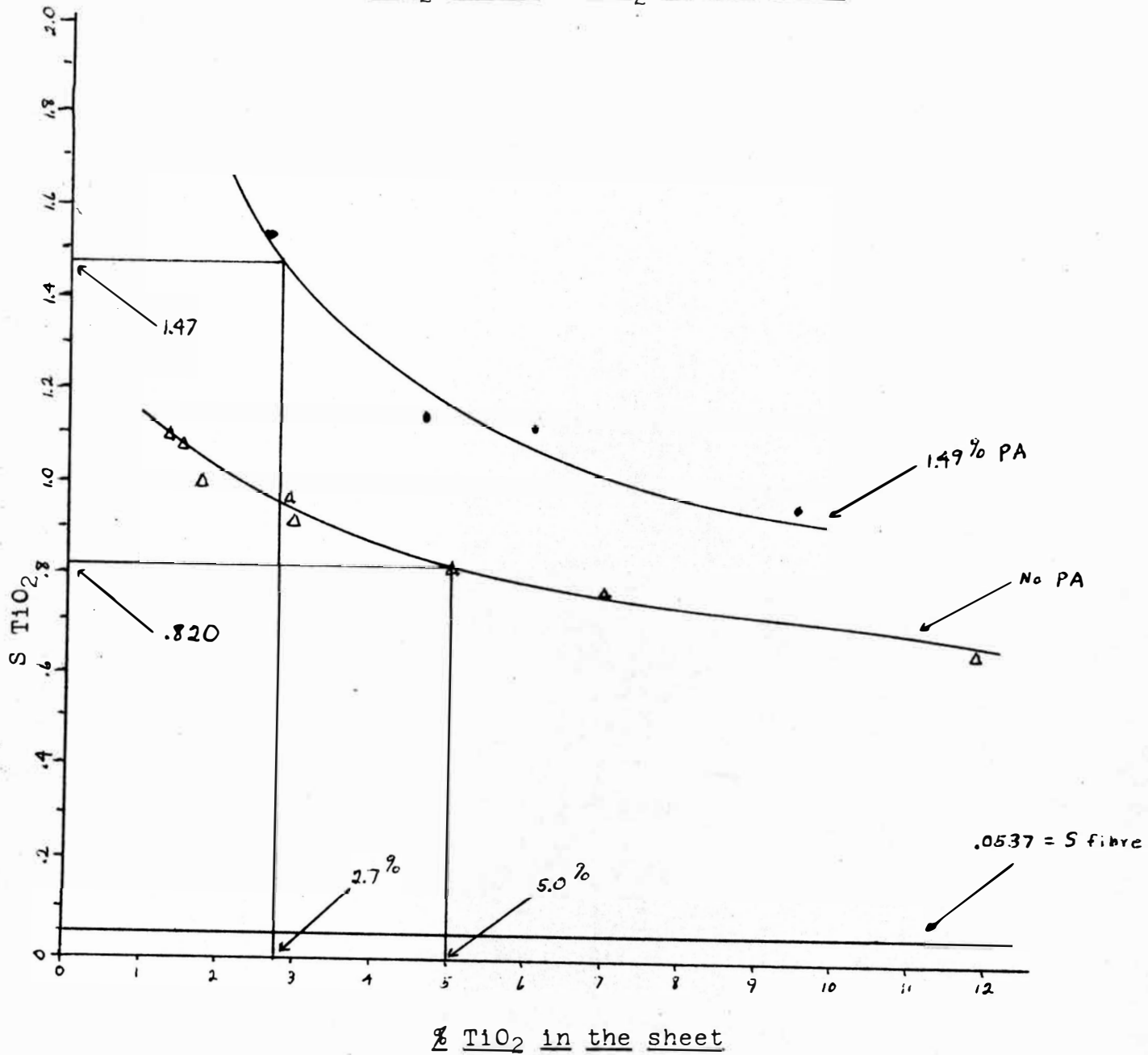
S TlO<sub>2</sub> versus % TlO<sub>2</sub> in the sheet





# GRAPHICAL ANALYSIS FOR ECONOMIC ANALYSIS

S TiO<sub>2</sub> versus % TiO<sub>2</sub> in the sheet



## ECONOMIC ANALYSIS OF RESULTS

### I. Comparison of co-dispersed $TiO_2$ with 1.30% PA to $TiO_2$ with 1.30% PA that is not co-dispersed.

A. Page IX of the appendix shows that if one were making paper which is 5%  $TiO_2$  that is not co-dispersed, he could achieve the same SX value with 4.2%  $TiO_2$  which has been co-dispersed

B. Arithmetical verification.

$$\begin{array}{rcl} .042(.805) + .958(.0490) & = & .050(.678) + .950(.0490) \\ .0338 + .0470 & = & .0339 + .0466 \\ & & .0808 = .0805 \end{array}$$

C. Calculation of savings per ton of paper which is 5%  $TiO_2$ .

$$\begin{array}{l} \text{Cost } TiO_2 = \$500/T \\ \text{Cost Pulp} = \$150/T \end{array}$$

$$\begin{array}{l} \text{Savings}/T = -.042(500) - .958(150) + .050(500) + .950(150) \\ = \$3.50/T \end{array}$$

### II. Comparison of $TiO_2$ co dispersed with 1.49% PA to $TiO_2$ that has not been treated.

A. Page X of the appendix shows the % of the treated  $TiO_2$  needed to give the same SX as un-treated  $TiO_2$ .

B. Arithmetical verification.

$$\begin{array}{rcl} .027(1.47) + .973(.0537) & = & .050(.820) + .950(.0537) \\ .0400 + .0523 & = & .0410 + .0511 \\ .923 & = & .921 \end{array}$$

C. Savings per ton of paper which is 5%  $TiO_2$ .

$$\begin{array}{l} \text{Cost } TiO_2 = \$500/T \\ \text{Cost fibre} = \$150/T \\ \text{Cost PA} = \$3.30/lb. \end{array}$$

$$\begin{array}{l} \text{Savings} = .050(500) + .95(150) - .027(500) - .973(150) \\ \quad \quad \quad - 2000(3.3)(.027)(.0149) \\ = 167.5 - 161.5 \\ = \$6/T \end{array}$$

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