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The Effect of Anthraquinone in the Kraft Pulping Process

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"THE EFFECT OF ANTHRAQUINONE IN THE KRAFT PULPING PROCESS"

Submitted to fulfill the
requirments of the coarse :
PAPER 470

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TABLE OF CONTENT.

STATEMENT OF PURPOSE.

Due to current attitudes and regulations concerning the odorous emission of mercaptans from the Kraft pulping process, new technology must be developed to enable the process to be run at lower sulfide levels. The use of cyclic-keto compounds, as pulping catalyst, could be a major step in the reduction of sulfide levels in Kraft pulping, while acting to increase the pulping yield through a mechanism that stabilizes the carbohydrates during the process and catalyzes delignification.

The objective of this research prodject is to evaluate the performance of one cyclic-keto compound that has recently recieved the attention of many researchers; Anthraquinone.

<u>Cyclic-keto compounds:</u>

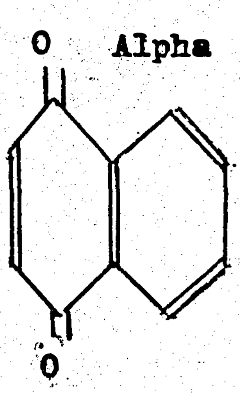
Many new methods and reagents have been devised to improve pulping yields by protecting the polysaccharides from degradation, such as the peeling reaction. The new reagents that have been found effective, such as sodium borohydride(20) or hydrazine(21) are too expensive to be applied economically. Sulfur compounds appear to be the major reagents that are widely used.

Four cyclic-keto compounds that have recently recieved a great deal of attention, in their use as pulping catalyst. They are Naphthoquinone, Anthraquinone, Anthrone, and Phenanthrenequinone.(14)

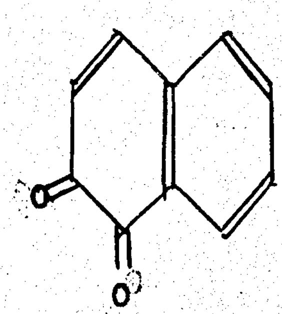
Naphthoquinone: ($C_{10}H_6O_2$)

This compound can be obtained in a beta(1,2) or an alpha(1,4) form. The beta form appears as orange-red crystals, which are soluble in water, ether, benzene, and alcohol. The alpha form appears as a greenish-yellow powder, and is soluble in water, ethanol, ethyl-ether, chloroform, benzene, and acetic acid. Both are considered to be moderately toxic, and an irritant.(16) The Naphthoquinone stuctures appear as shown below:(19)

Alpha

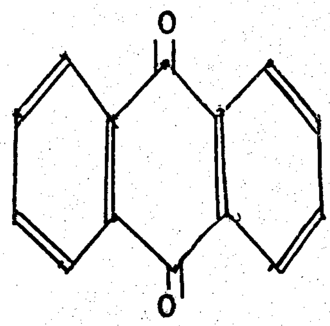


Beta



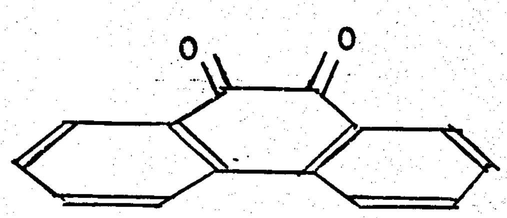
Anthraquinone: $(C_6H_4-CO_2-C_6H_4)$

This compound exist as yellow needles and is soluble in alcohol, ether, and acetone. It is insoluble in water. It is considered combustible, and has a low toxicity rating.(16) The anthraquinone structure appears as shown below:(19)



Phenanthrenequinone: $(C_{14}H_8O_2)$

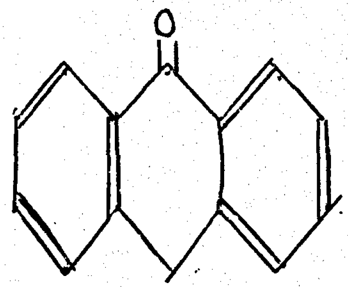
This compound appears as yellow-orange needles and is soluble in sulfuric acid, benzene, glacial-acedic acid, hot alcohol, and ether. It is insoluble in water.(16) The Phenanthrenequinone structure is shown below:(19)



Anthrone: $(C_{14}H_{10}O)$

This compound appears as colorless needles and is soluble in alcohol, benzene, and hot sodium-hydroxide. It is insoluble in water.(16) The Anthrone structure

is shown below: (19)



Comparison of effectiveness.

Previous work has been done to compare the effectiveness of cyclic-keto compounds as a catalyst for the Kraft and Soda pulping of softwoods. (4)

Soda process:

This process consisted of a one hour temperature rise to 180°C, and holding for 50 minutes at that temperature. The liquor was 20% sodium-hydroxide and 1% additive, based on a wood mixture of spruce, balsam fir, and pine. (4)

Name of Additive	Kappa No.	% Yield
Control	105.0	55.3
Naphthoquinone	80.0	52.5
Anthraquinone	27.5	51.1
Phenanthrenequinone	56.3	51.2
Anthrone	48.4	51.4

All of the cyclic-keto compounds had a positive effect on the Soda process. But it is evident that Anthraquinone was the best catalyst for the delignification of softwoods.

Kraft process:

This process consisted of a one hour temperature rise to 170 C, and holding there for 84 minutes. The liquor contained 12% active alkali on wood, 25% sulphidity, and 1% additive on a wood mixture of spruce, balsam fir, and pine.(4)

Name of Additive	Kappa No.	% Yield
Control	88.2	57.4
Naphthoquinone	72.0	54.6
Anthraquinone	47.0	54.7
Anthrone	63.1	54.4

The three additives all appear to increase the delignification capabilities of the Kraft process. Anthraquinone again shows the best results of all the additives tested.

Anthraquinone.

Anthraquinone appears to dominate the cyclic-keto compounds in delignification effectiveness, for both the Soda and Kraft pulping process. Therefore, the remainder of this thesis will be concerned with only Anthraquinone.

Anthraquinone has been used successfully in many laboratory pulping prodjects. As previously disscussed, both the Kraft and Soda processes benefit from the addition of Anthraquinone to the pulping liquor.(4)

It has been determined that the yield of an alkaline pulping process can be increased by pre-treating the stock(before contacting the liqour) with an alkaline solution of an alkalai metal salt of an anthraquinone sulfonic acid. The pre-treatment liquor is drained off and aeriated to re-oxidize the anthrahydroquinone sulfonate that is formed, back into anthraquinone sulfonate. There have been yield increases of up to 7.6% from the application of this pre-treatment.(8)

A high-yield pulping process has been developed using an alkaline pulping liquor containing anthraquinone mono- or di- sulfonic acid. This is followed by oxygen de-lignification to give pulp yields of 55 to 65 %.(9)

Experiments in which anthraquinone sulfonates were added to Soda and Kraft pulping liquors at levels of 3 to 5 %, showed that pulp yield levels increased from under 44 %, to over 51 %. Also, rejects were reduced to under 1 %. The resulting pulps were brighter, with a higher tensile strength, but a lower tear strength.(10)

Research work has shown that Anthraquinone also has potential in the sulfite process. Six-hundred grams of softwood chips were cooked in a calcium based sulfite liquor(total acids 7%, combined acids 1%) at a liquor to chip ratio of five to one, with the addition of .03 grams

of Anthraquinone. The cook lasted 8 hours at 180° C, to give a yield of 51.2 % and a Roe No. of 3.5 . An identical cook, without the Anthraquinone, gave a pulp yield of 47.2 % and a Roe No. of 4.6 .(12)

Possible mechanism of Anthraquinone.

Higher pulp yields are achieved by using a shorter cooking time to reach a desired level of residual lignin. This is possible due to the Anthraquinone acting to catalyze the delignification.

There is also some evidence to show that Anthraquinone acts to protect the carbohydrates from the degradation of the peeling reaction. It has been proposed that the addition of Anthraquinone leads to the oxidation of reducing-carbohydrate end groups in celluose and hemi-celluose, to produce aldonic-acid end groups which are more stable to the alkaline peeling reaction.(3)

		Anthraquinone	
Alkaline-Stopping Acids	Blank	0.1 %	1.0%
3-Deoxy-ribo-hexonic	9.9	9.8	5.8
3-Deoxy-arabino-hexonic	6.7	6.3	5.0
3-Deoxy-erythro-pentonic	1.8	2.0	1.2
3-Deoxy-threo-pentonic	2.3	2.6	0.8
2-C-Methylglyceric	11.7	10.3	3.1
Aldonic Acids			
Gluconic	5.0	6.5	14.6

Aldonic Acids(continued)	Blank	Anthraquinone 0.1%	Anthraquinone 1.0%
Mannonic	2.0	3.9	16.0
Altronic	-	-	0.7
Arabinonic	1.0	-	0.6
Xylonic	3.6	7.7	9.9
Lyxonic	2.5	5.9	8.6
Erythronic & Threonic	0.3	[illegible]	0.2

The above values represent milligrams of acid per 100 grams of pulp.(3) These values show a decrease in alkaline-stopping-reaction acids with a high(1%) and low(0.1%) addition of Anthraquinone. An increase in aldonic acids is aslo observed and helps to substantiate the theory of carbohydrate stabilization due to the addition of Anthraquinone.

Kraft pulping with Anthraquinone.

Research has been done at the laboratory, pilot mill, and a full-scale pulp mill to evaluate the effectiveness of Anthraquinone in the Kraft process.(1)(6)

The mill trial concerned four batch digesters, which were computer controlled. Anthraquinone was added at .05 % based on the wood. The additive was sprinkled on top of the southern pine chips as they passed through a chip conveyor.(1)

The resulting pulps demonstrated that with the addition of .05 % Anthraquinone, one could reduce the cooking time by 25 to 35 %, while producing an equivalent quality pulp,

as one would obtain using the same process, but without Anthraquinone. This can be seen in the data below: (1)

		Time(as H-factor)			
Cook #	Temp.(°F)	Rise	Run	Total	Kappa No.
671-688	169.7	114.0	652.8	766.8	66.1
692-703*	168.7	102.0	406.2	508.2	66.9
704-709	167.9	109.0	525.1	634.1	60.0
710-715	170.4	135.0	475.8	610.8	66.2
704-715	169.2	127.0	503.1	630.1	63.1

*indicates cooks with anthraquinone(.05% on wood)

In the mill trial, no unacceptable effects of Anthraquinone on the pulping equipment were detected. The recyling of the black liquor resulted in further Kappa Number reduction, indicating that the required level of Anthraquinone addition may be lower then previous laboratory studies have shown. (1)

Work that was done to compare the effectiveness of Anthraquinone and Anthraquinone mono-sulfonate in the Kraft processing of hardwoods, showed that Anthraquinone was the more effective catalyst, at a .05% addition level. Increased burst and tensile strengths were also noticed in the pulp, along with a decrease in tear strength. (2)

Health and safety considerations.

Whenever new reagents are considered for industrial use, their health and safety effects must be examined. Anthraquinone is considered to be a mild irritant in the cases of skin and eye contact. Ingestion can range from highly toxic, to non-harmful, depending on the amount consumed. No reference to Anthraquinone is found in the following regualtions: (17)

1) U.S.A. Department of Transportation-"Hazardous materials regulations."
2) International Air Transport-"Restricted articles."

In handling, one should be aware that Anthraquinone is combustable, with a flash point of 185°C. The dust from this reagent is very sensitive to low energy electrostatic ignition, therefore dust generation and buildup should be avoided. (17)

Some consideration must be given to tracing the Anthraquinone in the mill. Mead Paper is presently using Anthraquinone in a Soda cook of hardwoods at Kingsport, Tennessee. They have traced the reagent and found that 95 % remains in the cooking liquor, and only 5 % stays with the pulp after washing. (7) This indicates that there should be negligible Anthraquinone in the finished paper, and that there are probable benefits from recycling a portion of the black liquor.

The standard method of determining Anthraquinone content of a celluose sample, is a spectrophotometric determination at 440 and 515 mμ. A long sequence of organic separation is required before the determination can be made. (18)(19)

Conclusions.

Enough research work has been done to substantiate the positive effect that cyclic-keto compounds have on the pulping process. Anthraquinone appears to outperform the other cyclic-keto compounds in alkaline pulping processes. in catalyzing the delignification reaction and protecting the carbohydrate end-groups from the peeling reaction.

More research must be done to determine the ability of Anthraquinone to replace sulfides, or at least lower the sulfides in the liquor, and still obtain a high quality pulp. Research is also needed to determine if Anthraquinone may disrupt the Kraft liquor regeneration cycle.

Purposed experimental outline.

The student intends to compare the effectiveness of Anthraquinone on the Kraft process, while allowing the sulfide levels of the Kraft liquor to vary. The intent is to find if lower sulfide levels can be used and still obtain a quality pulp. Some variation of the Anthraquinone levels is also planned, to determine if any interaction occurs between the two reagents.

The M & K laboratory digester will be used to cook softwood chips at approxomately 170°C, for 1.5 hours. Anthraquinone is to be added at .05 , .1 and 1.0 % based on wood. The liquor will contain 12% active alkalai, and sulphidity in the range of 10 to 25 %. All of the resulting pulps will be tested for % yield, Kappa No., and viscosity.

If time allows, some effort will also be made to analyze the amount of Anthraquinone left in the pulp after washing. A spectrophotometric determination will be attempted as in reference (18).

Cook Number	% Anthraquinone	% Sulphidity
1	0	0
2	.05	0
3	.10	0
4	1.0	0
5	0	5
6	.05	5
7	.10	5
8	1.0	5
9	0	10
10	.05	10
11	.10	10
12	1.0	10
13	0	15
14	.05	15
15	.10	15
16	1.0	15
17	0	20
18	.05	20
19	.10	20
20	1.0	20
21	0	25
22	.05	25
23	.10	25
24	1.0	25
25		

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Table of Content.

Statement of Purpose.

This experiment is designed to evaluate the effectiveness of Anthraquinone in the Kraft cooking of softwoods,,at different sulfide levels. Previous work has shown that anthraquinone acts to increase the pulping reaction at very low sulfide levels. However, anthraquinone had very little effect at high sulfide levels(15%-45%), as can be seen in graph one in the appendix.(5)

Description of Experimental Work.

Three-hundred and forty-eight grams (bone-dry weight) of assorted softwood chips were cooked in a M/K system's Mini-Mill Laboratory Digester. The chips contained 22.5 % moisture.

The M/K digester is designed for laboratory research in pulping. It has a 4.7 litre cooking vessel, fitted with a basket to hold the chips. The liquor is circulated at a controlled rate down over the chips using a Dyna-pump and passing through a heat exchanger. The maximum operating conditions obtainable are 150 psi and 186°C.(4)

After the chips were placed into the digester, they were sprinkled and mixed with finely powdered anthraquinone. The anthraquinone was added as a percentage of the (bone-dry) weight of chips.

The cooking liquor was prepared to achieve 16% active alkalai expressed as Na_2O. It was determined nessesary to increase the active alkalai from 12% to 16% in order to obtain better cooking conditions. A six-to-one liquor ratio was used, because a four-to-one liquor ratio did not provide enough liquor to circulate properly.

After the 2014 ml of cooking liquor were added, the digester's pump was activated to insure liquor circulation. Then a small amount of grease was applied to the o-ring on the cover, and the cover was placed over the digester and tightened down using the hand screws.

The cooks lasted one and one-half hours at 170°C and 108 to 112 psig. It took about one hour to attain these cooking conditions. Air was bled off at lower temperatures to achieve optimum cooking conditions. Both the continuous heater and the control heater were used to attain and maintain the cooking conditions.

At the end of the cooking period, both heaters and the digester pump were turned off. A small sample of cooking liquor was collected through a condenser that was attached to the bottom drain of the digester. The pressure was then released through the top valve of the digester. The chips were removed from the digester and washed with water while still in the chip basket.

Pulp Handling:

After washing the liquor off the chips, they were defibered in a Waring blender for one minute. The stock was then washed and screened carefully. Pulp yields were obtained as in TAPPI standard(3) for the stock both before and after defibering and washing. The yields shown in the experimental data were obtained after washing, defibering, and screening.

Kappa Number:

Kappa numbers were determined in duplicate for all twelve cooks, as described in TAPPI standard(1). The data page reports the mean Kappa number value. A Kappa number gives one an indication of how much Klason lignin

remains in the pulp, as an indication of the effectiveness of the cook.

Pulp Viscosity

A measure of the pulp's viscosity would have been useful in observing the relative degradation of the cellulose in the pulps. However, the student was unable to properly prepare the Cupriethylenediamine solution required for this determination.(2)

Conclusions:

The data for the pulp yields show clearly that the addition of anthraquinone will act to lower the yield by increasing the pulping reaction. Anthraquinone also appeared to be more effective in soda and low sulfide cooks, then in higher sulfide cooks. This can be seen in graphs two and three in the appendix.

The data for the Kappa numbers gives a good indication that anthraquinone will act to increase delignification in the soda cooking process. However, it does not perform as clearly in the Kraft cooks. Low sulfide cooks(5%) appeared to benefit from anthraquinone, while the Kappa numbers of the high sulfide cooks(20%) appeared to increase from the addition of anthraquinone. This can be seen in graphs four and five in the appendix.

All of the graphed data indicate some type of interaction between the levels of sulfide and anthraquinone.

It is the conclusion of the student that anthraquinone acts to increase the pulping reaction, but may be accomplishing this by cellulose degradation in the Kraft cooks, rather then acting only to aide in delignification.

High yields(70% plus) could have introduced error into the determination of Kappa numbers. Harsher cooking conditions would have helped to lower the yields, and give a wider range to the data.

EXPERIMENTAL DATA:

RUN	% AQ.	% Sulfidity	% Yield	Kappa No.
1	0.0	0.0	76.5	82.5±1
2	0.5	0.0	75.9	80.0
3	1.0	0.0	64.5	72.4
4	0.0	5.0	70.8	73.7
5	0.5	5.0	70.5	67.3
6	1.0	5.0	69.0	71.6
7	0.0	10.0	72.9	77.1
8	0.5	10.0	68.7	75.1
9	1.0	10.0	68.6	75.1
10	0.0	20.0	73.3	65.4
11	0.5	20.0	72.0	78.7
12	1.0	20.0	72.0	76.8

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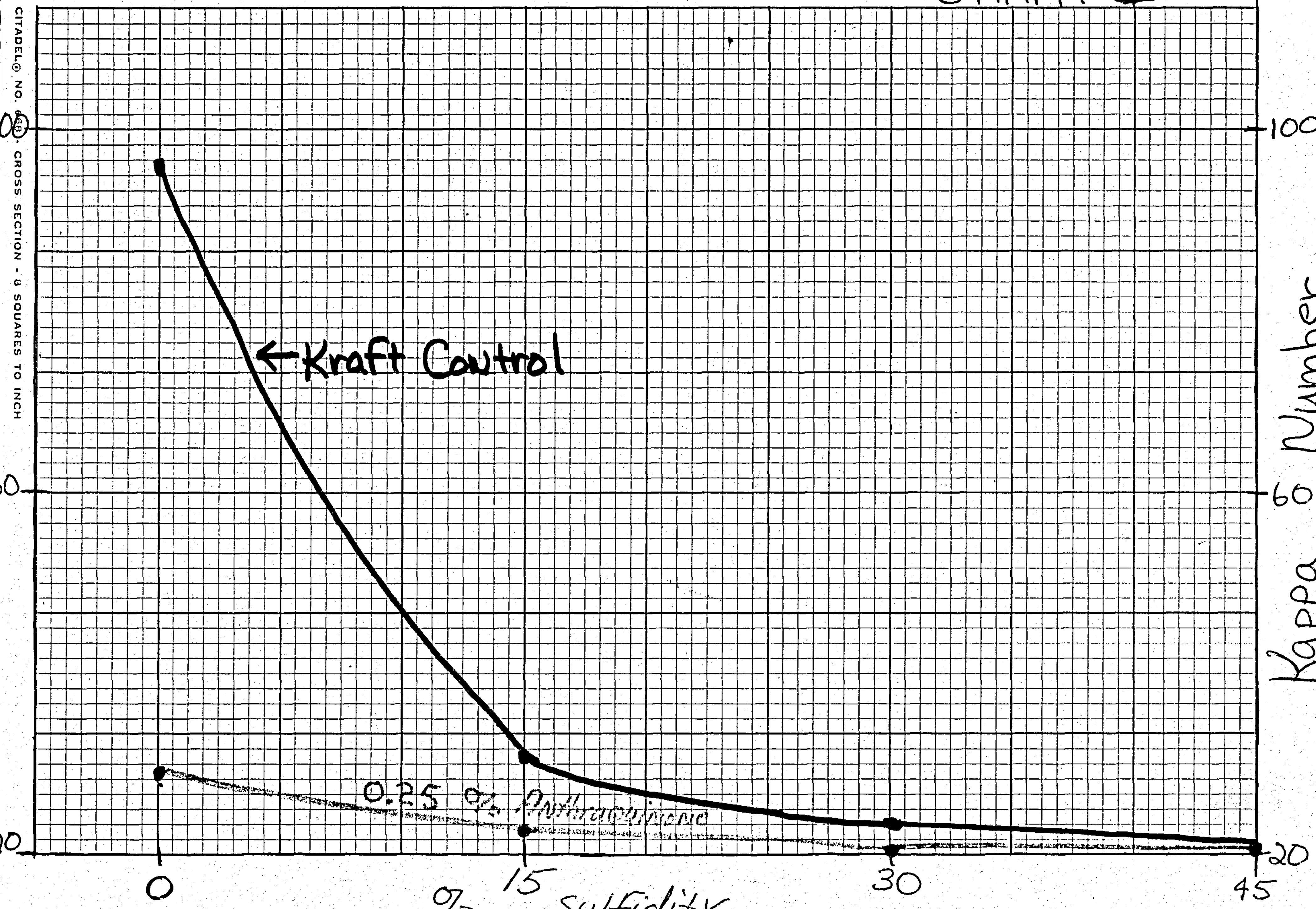
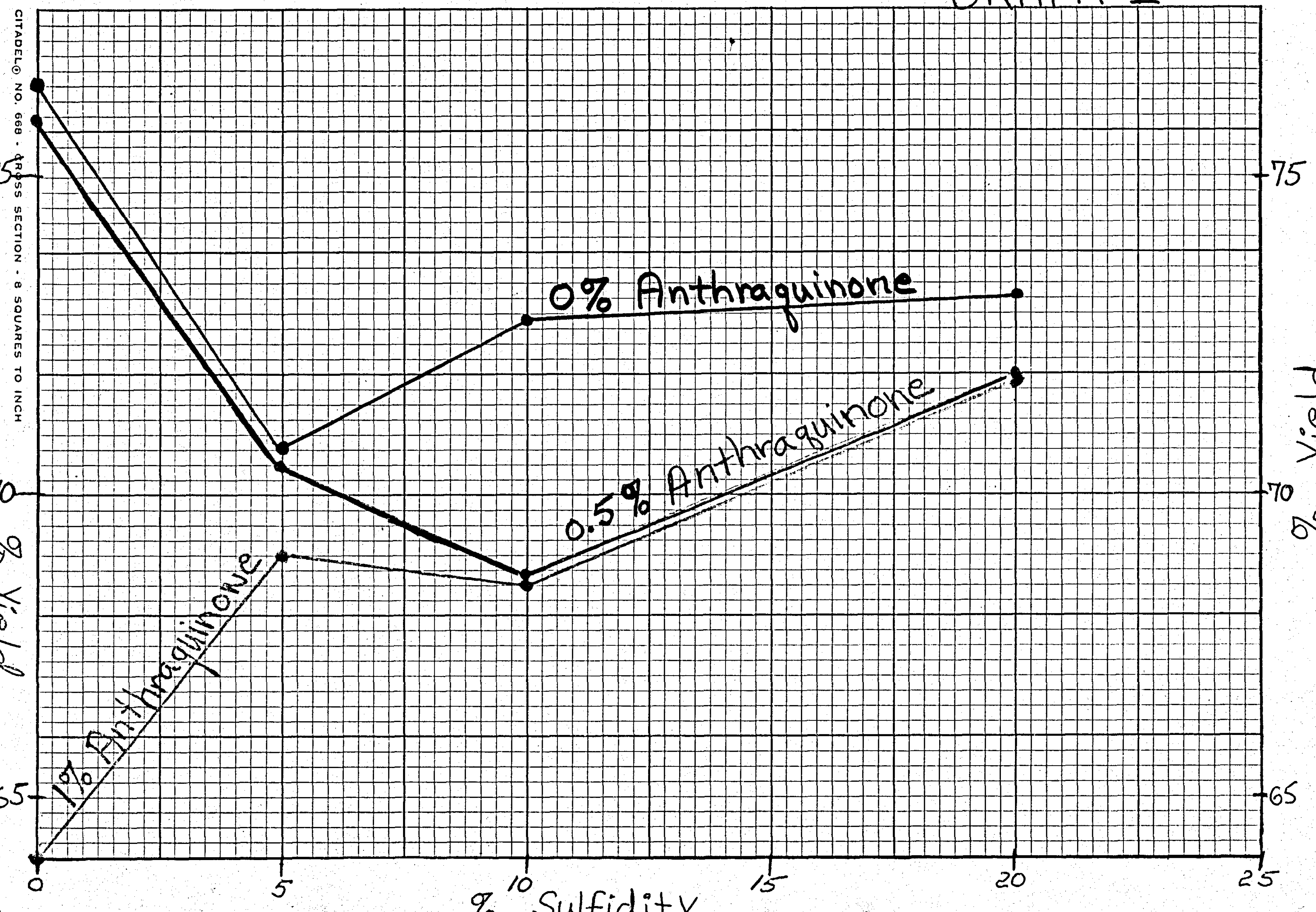
GRAPH 4

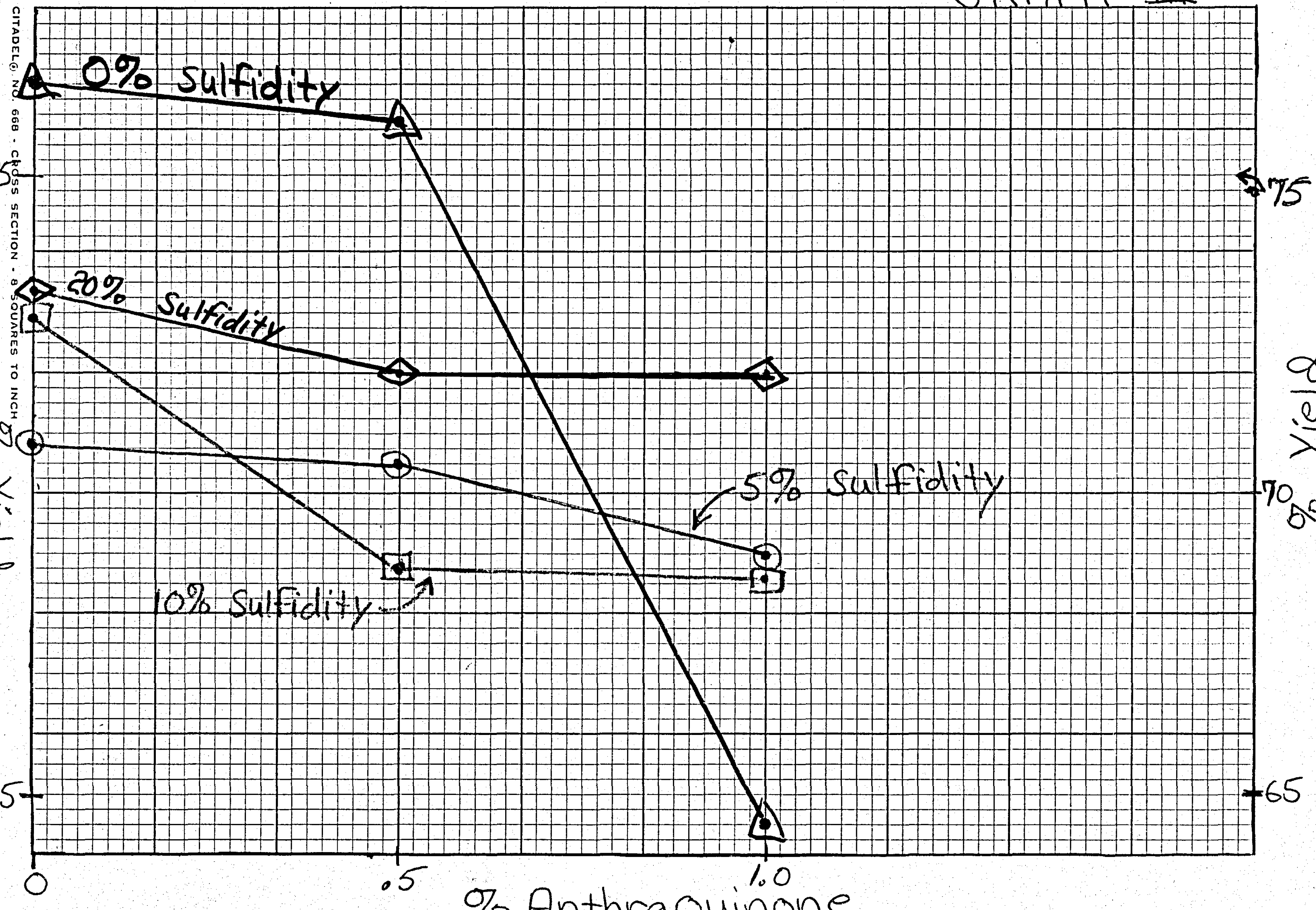


←Kraft Control
0.25 % Anthraquinone
Kappa Number
100
60
20
0
15
30
45
% sulfidity

GRAPH II


0% Anthraquinone
0.5% Anthraquinone
1% Anthraquinone
0
5
10
15
20
25
% Sulfidity
75
70
65
% Yield
CITADEL® NO. 668 - CROSS SECTION - 8 SQUARES TO INCH

GRAPH III



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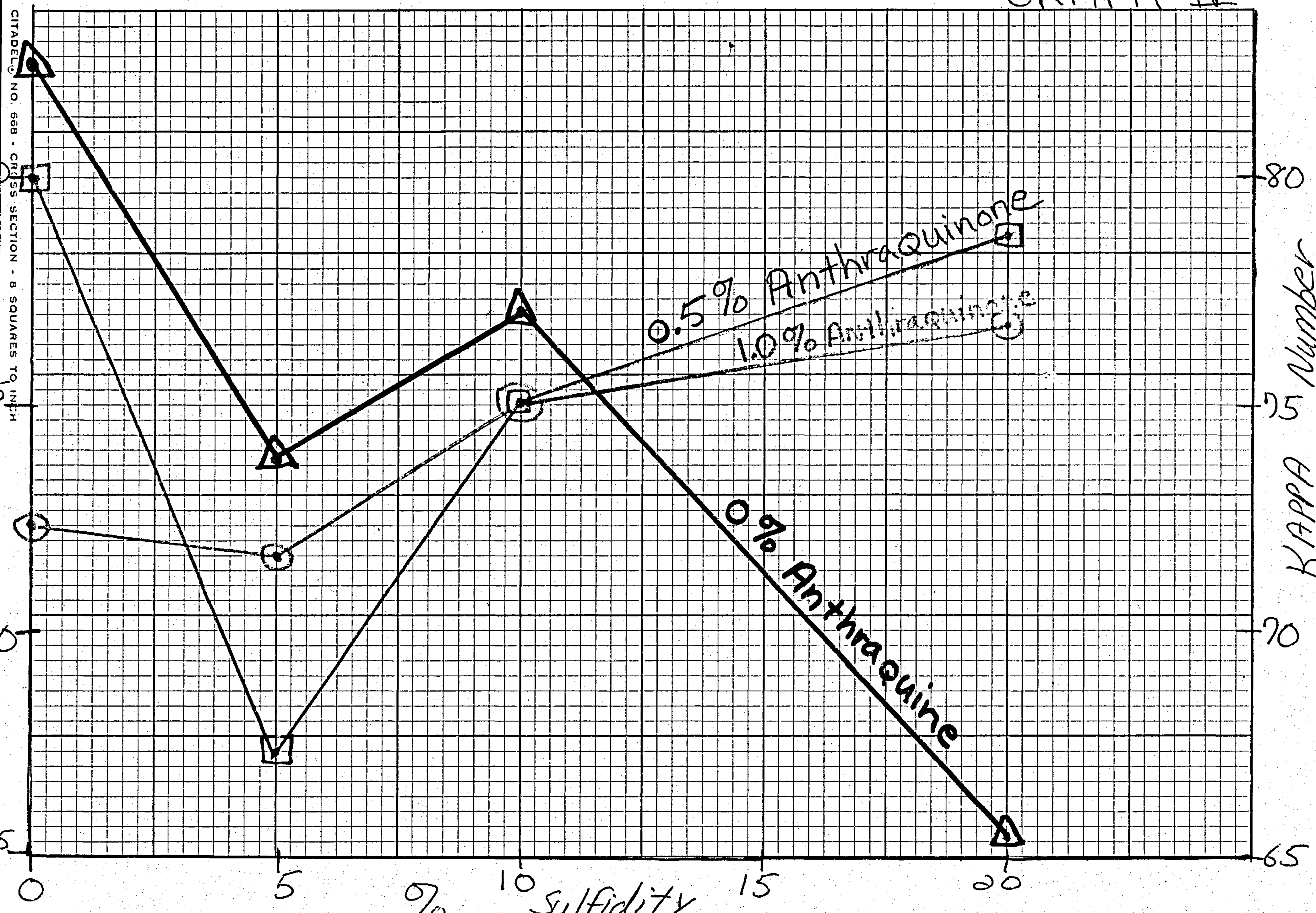
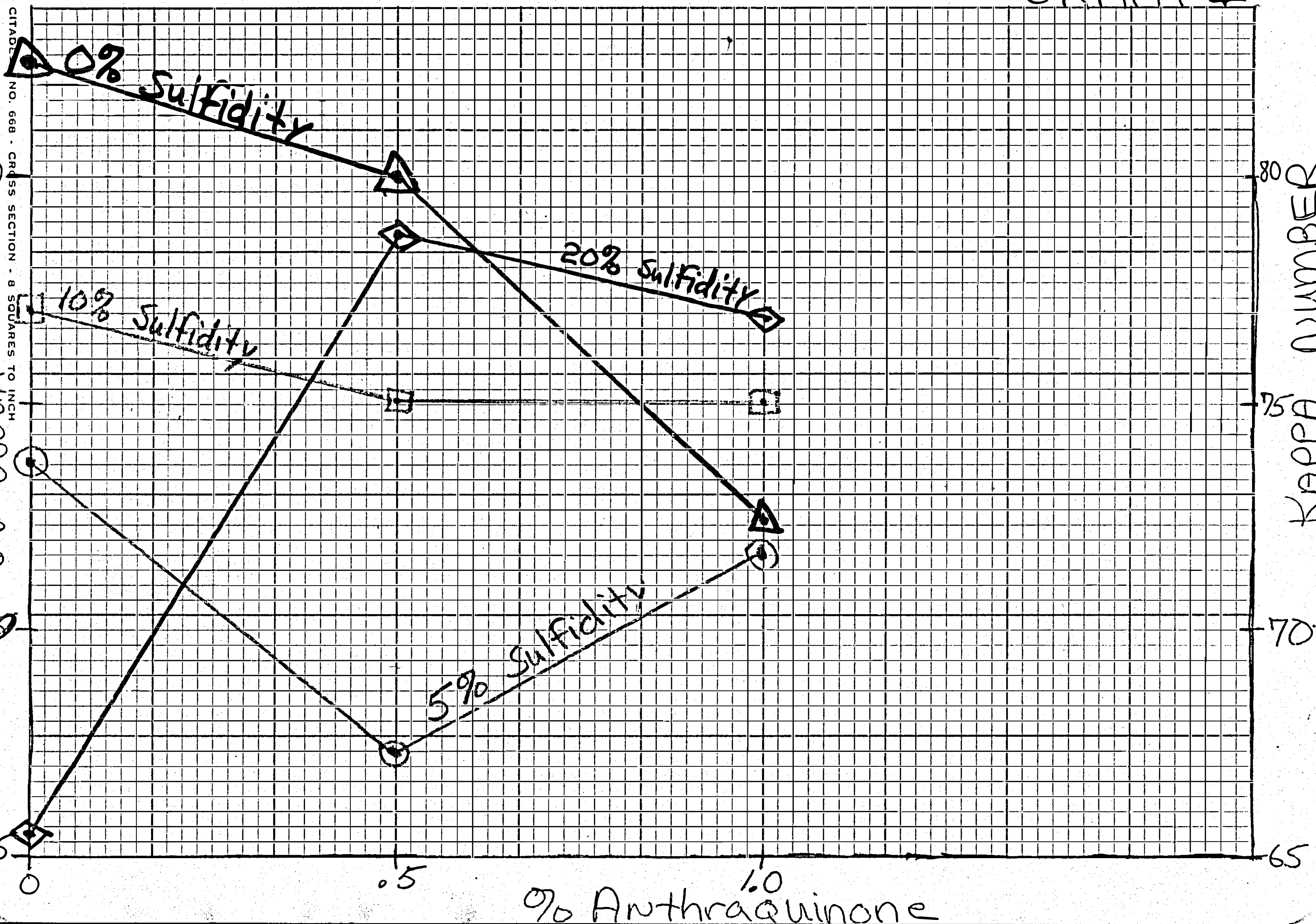
GRAPH IV



0.5% Anthraquinone
1.0% Anthraquinone
0% Anthraquine
KAPPA Number
80
75
70
65
0
5
10
15
20
% Sulfidity
CITADEL NO. 668 - CROSS SECTION - 8 SQUARES TO INCH

GRAPH V



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