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Effectiveness of Aluminum Sulfate and Ethylenediamine Tetraacetic Acid as Carbohydrate Protectors during Oxygen Delignification

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EFFECTIVENESS OF ALUMINUM
SULFATE AND ETHYLENEDIAMINE
TETRAACETIC ACID AS CARBOHYDRATE
PROTECTORS DURING OXYGEN
DELIGNIFICATION

For:

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By

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PAPR 473 Senior Engineering Design

WESTERN MICHIGAN UNIVERSITY

KALAMAZOO, MICHIGAN

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OBJECTIVE

The purpose of this thesis will be to examine three carbohydrate protector's effectiveness during oxygen delignification. Today, about half of the lignin can be removed from a conventional kraft pulp through the application of oxygen delignification as an initial stage in the bleaching process. More extensive delignification results in the degradation of pulp carbohydrates, influencing the final pulp qualities.¹ Carbohydrates are attacked by the decomposition of hydroperoxides catalyzed by heavy metal ion, free radicals. Carbohydrate protectors function to deactivate the free radicals, reducing the rate of attack on the carbohydrates.² This thesis is based on the above principle. The carbohydrate protectors for comparison are Ethylenediamine Tetraacetic Acid (EDTA), Aluminum Sulfate [$Al_2(SO_4)_3$] and Magnesium Sulfate [Mg_2SO_4].

Oxygen-alkali delignification of unbleached kraft softwood pulp was performed using a pressurized autoclave. The effectiveness of the above agents as carbohydrate protectors involved intrinsic viscosity and brightness comparisons of oxygen-delignified pulp with and without the presence of a protector. Viscosity provides an indication of fiber degradation, resulting from the delignification process. Brightness was used as a confirmation of the delignification. The viscosity and brightness values obtained for pulps treated with $Al_2(SO_4)_3$ and EDTA were compared to base stock samples with and without the protection of magnesium sulfate. Magnesium sulfate is accepted in industry as an

effective carbohydrate protector.

BACKGROUND

Pulp fibers, as they are obtained from chemical or mechanical digestion, are distinctly colored anywhere from dark brown to a creamy white. This color is a result of the chromophoric complexes formed by the phenolic groups of the lignin molecules. The whiteness of a given pulp sample is measured by its ability to reflect monochromatic light as compared to a known standard (commonly magnesium oxide).³ It is believed that the oxidative mechanisms convert portions of the phenolic groups to quinone-like substances that are known to absorb light. In order to produce a "white" pulp these lignin compounds must be chemically altered, or decolorized. Hence the principal objective of bleaching is the reduction of the color creating constituents.

Oxygen bleaching was developed and implemented for many reasons. The development of oxygen bleaching has been driven by economic, environmental, and energy related considerations. The increasingly stringent environmental requirements have led to the development of oxygen bleaching as a method of delignification. Oxygen delignification is a commercially proven technology for reducing bleach plant effluent.⁴ Probably most significant, oxygen bleaching involves no chlorine compounds, and therefore is not overly detrimental to the environment. Significant reductions in bleach effluent BOD, color and organic chlorine compounds are realized by removing much of the lignin in the unbleached pulp before the chlorination stage. The dissolved material unlike that from chlorination and caustic extraction is uncontaminated by the

chlorine ion.⁵ Therefore, it may be routed directly back to the recovery furnace. It now becomes an energy source instead of a pollutant.

Secondly, economic and energy related benefits result from the use of oxygen bleaching. Economic savings arise from the reduction of chlorine, chlorine dioxide, and caustic. Chemical savings in the chlorination and the extraction stages are proportional to the amount of lignin removed during the oxygen stage. These savings are not negated by the cost of operating the oxygen stage itself because the source of alkali in this stage can be oxidized white liquor. The oxygen required is cheaper than the chlorine that it replaces.⁶ One might presume that chlorine dioxide savings from the later stages result from the beneficial changes in the residual lignin structure brought about by its earlier exposure to oxygen.

Finally, the energy related benefits include recovery of heat from the burning of the waste material from the oxygen stage. The ever increasing solid waste load, increasing material values, and increasing energy costs are forcing a new appraisal of historical land disposal and/or incineration of the past. The organic portion which is comprised to a great extent of paper fiber is usually burned or placed into sanitary landfills.⁷ While paper is considered a value as a fuel source, upgrading it could increase its value and reduces wasted fiber sources in the future. Oxygen bleached pulps require less energy to refine, therefore reducing energy consumption. The manufacture of oxygen only requires approximately one eighth of the energy required to produce a

chemically equivalent amount of chlorine. •

LITERATURE REVIEW:

Russian scientists were the first to effectively demonstrate that an oxygen-caustic soda pulp pretreatment provided considerable delignification of unbleached pulps. They determined that this was not a bleaching, but a delignification stage used prior to bleaching.⁹ The caustic soda initially acts as a swelling agent, improving the accessibility of the oxygen to the pulp. Alkali promotes the formation of carbanions which constitutes the sites of attack by oxygen.¹⁰ The use of oxygen results in fragmentation of the lignins or formation of conjugated chromophoric structures. During the above process two competing reactions, delignification and carbohydrate degradation occur simultaneously.¹¹

Oxygen can be used for "true bleaching," most installations use the alkaline oxygen stage as a delignification step prior to bleaching with chlorine chemicals. Most commercial uses are performed at 20.0 % to 30.0 % consistency, however, a new method found uses 3.0 % to 5.0 % consistency pulp and gaseous caustic and oxygen are added at intervals without a magnesium protector or cellulose degradation. This process is limited by the amount of cellulose degradation that is tolerable.¹²

By looking at the above benefits one can obviously see that oxygen bleaching has become a well established process. The oxygen stage effluent is totally compatible with the kraft liquor recovery system. Therefore, bleach plant effluent loading is greatly diminished while the soda is recovered. Alkali in the oxygen stage neutralizes organic acid reaction products to maintain a higher pH,

magnesium salt serves as a protector of cellulose degradation.

CHEMISTRY OF THE BLEACHING PROCESS

Lignin Reactions:

The mechanism responsible for the removal of the residual pulp lignin by bleaching agents is not known in detail and many of the explanations offered will be to some degree speculative. This can be understood in view of the complex structure of the residual lignin, which also varies depending on pulping method.¹³ The reactions between oxygen and lignin are exceedingly complex as a result of the large number of competing reaction pathways. Pathways available during the oxidation process include side chain displacement, oxidative coupling, formation of epoxidated quinol structures, and ring cleavage between methoxyl bearing ring carbon and either of adjacent ring carbons.¹⁴ Each of the above pathways may lead directly to the modification and degradation of phenolic moieties in lignin. Significant reactions of lignin are initiated when a phenolic hydroxyl group in the lignin reacts with alkali to form a phenolate ion. The oxygen molecule has two higher energy cells levels (single state) characterized by two paired or unpaired electrons with an antiparallel spin. Due to its unpaired electrons oxygen participates in chain reactions. Radicals may be generated by electron abstraction from phenolate ions (in lignin) giving rise to resonance-stabilized phenoxy radicals or directly by abstraction of the hydrogen atoms linked to the carbon. The oxygen then reacts with these ions to form reactive intermediates which are called hydroperoxides. Small quantities of transition metal ions will

catalyze the decomposition of the hydroperoxides into extremely reactive alkoxy or hydroxyl radicals that can abstract hydrogen atoms from carbohydrates resulting in their degradation. The intermediate then undergoes fragmentation by one of several individual pathways. These include reactions that break up the polymeric structure of the lignin molecule. Other reactions make the resulting fragments water soluble.¹⁶ Some components of the delignification process produce hydrogen peroxide, which can further react with both lignin and carbohydrates.

Carbohydrate Reactions:

The degradation of the carbohydrates is the chief factor limiting the amount of delignification that can be achieved in the oxygen stage.¹⁶ Carbohydrate degradation involves free radical processes in which peroxides and metal ions (such as iron, manganese, and copper) play an important part. In the presence of the above ions, free reactive radicals form that randomly attack links in the calisaya chains, breaking the chain at the point of attack. This reduces the pulp viscosity and if allowed to proceed far enough, may result in loss of pulp strength. The viscosity is sharply decreased when a pulp is delignified with an oxygen and alkali without any additives (inhibitors). [See FIGURE 1.0]¹⁷ The pulp polysaccharides are attacked by radicals generated by the decomposition of hydroperoxides catalyzed by heavy metal ions. Or possibly formed directly in the reaction of the oxygen with organic material. The peroxide decomposition is partly inhibited by the presence of other compounds, especially magnesium salts and

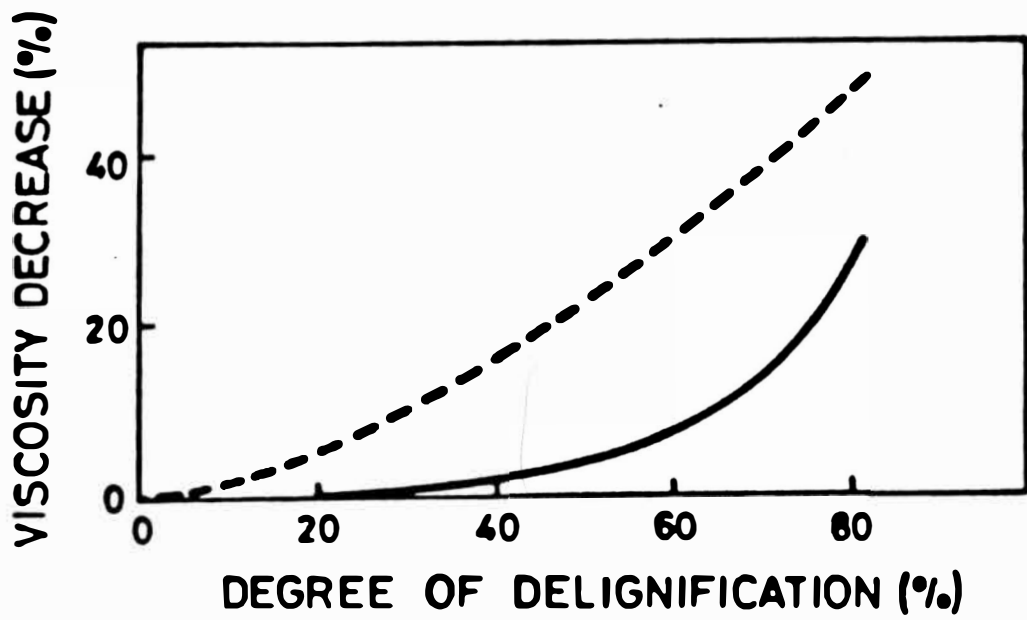


Figure 1.0. Depolymerization of cellulose (viscosity decrease) during oxygen bleaching of pine kraft pulp. Dotted line, no inhibitor addition; full line, inhibitor added (Mg salt).

triethanolamine, capable of deactivating the heavy metals. Because this attack is random, it is unlikely it will occur close enough to the chain end to produce a soluble, low molecular weight fragment.¹⁸

Peeling Reaction:

In the alkaline medium, the stage in which the yield is loss is called the peeling reaction, since it successively removes individual monomeric units from the cellulose chain end. An end group must contain a carbonyl group in order to be susceptible to removal by the peeling process. The stopping reaction converts the end unit to one that does not contain a carbonyl group, therefore preventing the continuation of the peeling process.¹⁹

Yield loss in a kraft pulp during an oxygen bleaching process is not a serious problem for two reasons. First, kraft pulps contain few end units that have not been converted to the stable form by the stopping reaction, as a result of their long exposure to the strongly alkaline conditions in the digester. The other reason is because the oxygen itself converts reducing end groups to stable oxidized forms. Peeling may be a problem if random chain cleavage is excessively abundant. This is due to the fact that chain cleavage creates a new chain end that now contains a carbonyl group.²⁰

Carbohydrate Protectors:

Carbohydrate protectors function to deactivate the heavy metal ions, thereby reducing the decomposing rate of the hydroperoxides. Two types of protectors, metal hydroxides and chelating agents are

used to inhibit degradation during oxygen delignification. The active component in the metal hydroxide is actually the metal hydroxide that is precipitated out of the reaction in the presence of an alkali concentration. This precipitated metal hydroxide has an inherently strong ability to absorb heavy metal ions in the solution. This reaction deactivates the heavy metal ions in turn decreasing the decomposition rate of the hydroperoxides. Magnesium sulfate and aluminum sulfate act as metal hydroxide inhibitors.²¹

The second type of degradation inhibitor is a chelating agent like ethylenediamine-tetraacetic acid (EDTA). A chelating agent is a molecule that contains two coordinating atoms positioned such that they may form a ring with a third atom or ion resulting in a chelate compound. (SEE FIGURE 2.0)²² The ring closing compound is held in a molecular claw. EDTA was used to hold the metal ions in solution, making the metal ions unable to catalyze the decomposition reaction of the hydroperoxides as readily.²³

One can loosely define selectivity as the ratio of attack on lignins to the attack on carbohydrates. As the amount of transition metals in the pulp increases the selectivity decreases. Metal ions such as iron, manganese, and copper facilitate the formation of reactive radicals that attack the cellulose chain links. Most all pulps contain some concentration of these metal ions. Possible carbohydrate protectors include magnesium salts, aluminum sulfate, and certain sequestering agents such as EDTA.

EXPERIMENTAL DESIGN

This project was designed to determine if the use of $\text{Al}_2(\text{SO}_4)_3$ (aluminum sulfate) and EDTA (ethylenediamine tetraacetic acid) during oxygen delignification will provide ample protection against carbohydrate degradation. The effectiveness of the above agents as carbohydrate protectors was determined using viscosity and brightness tests for comparison. The test values obtained for $\text{Al}_2(\text{SO}_4)_3$ and EDTA will be compared to base stock samples, with and without the protection of MgSO_4 . Magnesium sulfate being accepted by industry as an effective degradation inhibitor.

This experiment examines $\text{Al}_2(\text{SO}_4)_3$, MgSO_4 and EDTA at a 0.5% concentration on oven dried pulp. Variables that were held constant include temperature, pH, retention time, partial pressure of oxygen, and consistency. Recommended maximum temperature ranges were 120° Celcius and 7-9 percent alkali addition on oven dried pulp. Oxygen delignification out of the above range may be detrimental to the actual strength properties of the pulp. A partial pressure between 110-145 PSI is commonly suggested as an optimum pressure range.²⁴

High consistency delignification is performed in the 18-25 percent consistency range in industry. Delignification in the 8-16 percent consistency range is classified as medium consistency delignification. High and medium consistency delignification are the two prominent ranges used in industrial delignification. The delignification of medium consistency compared to low consistency (under 4 percent) pulp demonstrates a slightly lower

delignification. A review of delignification literature illustrates that 40-45 percent lignin removal is achievable at medium consistency. This can be compared to the 50-60 percent obtained at low consistency."

The benefit that low consistency delignification provide over high and medium consistency are as follows. Low consistency allows for a greater interfacial area of contact between the pulp fiber and the oxygen. This provides a more efficient delignification and fewer required bleaching stages. However, in industry, this advantage in delignification does not outweigh the cost resulting from the higher water load at low consistency.

Duplicate runs were made for each of five test specimens.

These specimens were tested as follows:

SPECIMEN A: Base stock - with no retention time
SPECIMEN B: Base stock - 45 minutes retention time
SPECIMEN C: $Al_2(SO_4)_3$ - 45 minutes retention time
SPECIMEN D: EDTA - 45 minutes retention time
SPECIMEN E: $MgSO_4$ - 45 minutes retention time

EXPERIMENTAL PROCEDURE

All procedures used during the experimentation were based upon current industrial practices. Chemical additions were based upon published values encountered during the literature review. The experimental processes will vary from industrial examples as a result of laboratory limitations. Seven distinct experimental stages have been set up to help illustrate the experimental process and are summarized below:

- STAGE 1: EQUIPMENT PREPARATION
- STAGE 2: PRE-EXPERIMENTAL STOCK-PREPARATION
- STAGE 3: CONSISTENCY DETERMINATIONS
- STAGE 4: RETENTION TIME DETERMINATION
- STAGE 5: STOCK PREPARATION
- STAGE 6: OXYGEN DELIGNIFICATION
- STAGE 7: PULP TESTING

STAGE 1: EQUIPMENT PREPARATION

The initial stage primarily involved researching related procedures and preparing the required equipment. For oxygen delignification, a Magnedrive II Autoclave was obtained from Western Michigan University's Chemistry Department. The autoclave was not designed for oxygen delignification of pulp fibers; therefore modifications were required so that oxygen delignification could be performed. Although not designed for delignification the Magnedrive II possessed the following favorable characteristic. The Magnedrive was rated to withstand temperatures up to 650^oC and pressures up to 4000 pounds per square inch (PSI). In addition, the Magnedrive II provides a mercury sealed shaft, powered by a quarter-horsepower electric motor. This rotating shaft supports an impeller to insure

circulation of stock under process conditions.

The magnedrive also possessed sample ports for the injection of the oxygen and the release of relief vapors. The addition of the oxygen to the Magnedrive II was accomplished by modifying the systems tubing. Tubing from an oxygen tank to the top of the Magnedrive II's sample ports provided oxygen feed. With the high pressure developed in the autoclave, a check valve was applied just before the oxygen line enters the digester (See Figure 3.0). With this modification it will be possible to monitor the partial pressure of the oxygen in the system during the bleaching process. The sample vessel is heated indirectly by an external surface furnace. A thermocouple was placed in an internal vessel tube and with the use of a digital temperature meter vessel temperature could be monitored.

At this point the autoclave was tested to see if it could maintain and withstand process conditions. A partial pressure of 120 PSI(g) of oxygen was maintained effectively by the vessel. Boiling water and a thermometer were used to determine the accuracy of the thermocouple unit. It was found after five trials that the thermocouple unit was within $\pm 0.5^{\circ}\text{C}$ of the thermometer.

STAGE 2: PRE-EXPERIMENTAL STOCK PREPARATION

An unbleached, kraft softwood pulp was obtained from the Western Michigan University's Paper Pilot Plant. This lap pulp was dispersed using a Valley Beater following the respective TAPPI STANDARD procedure using distilled water. Distilled water was used

MAGNEDRIVE AUTOCLAVE

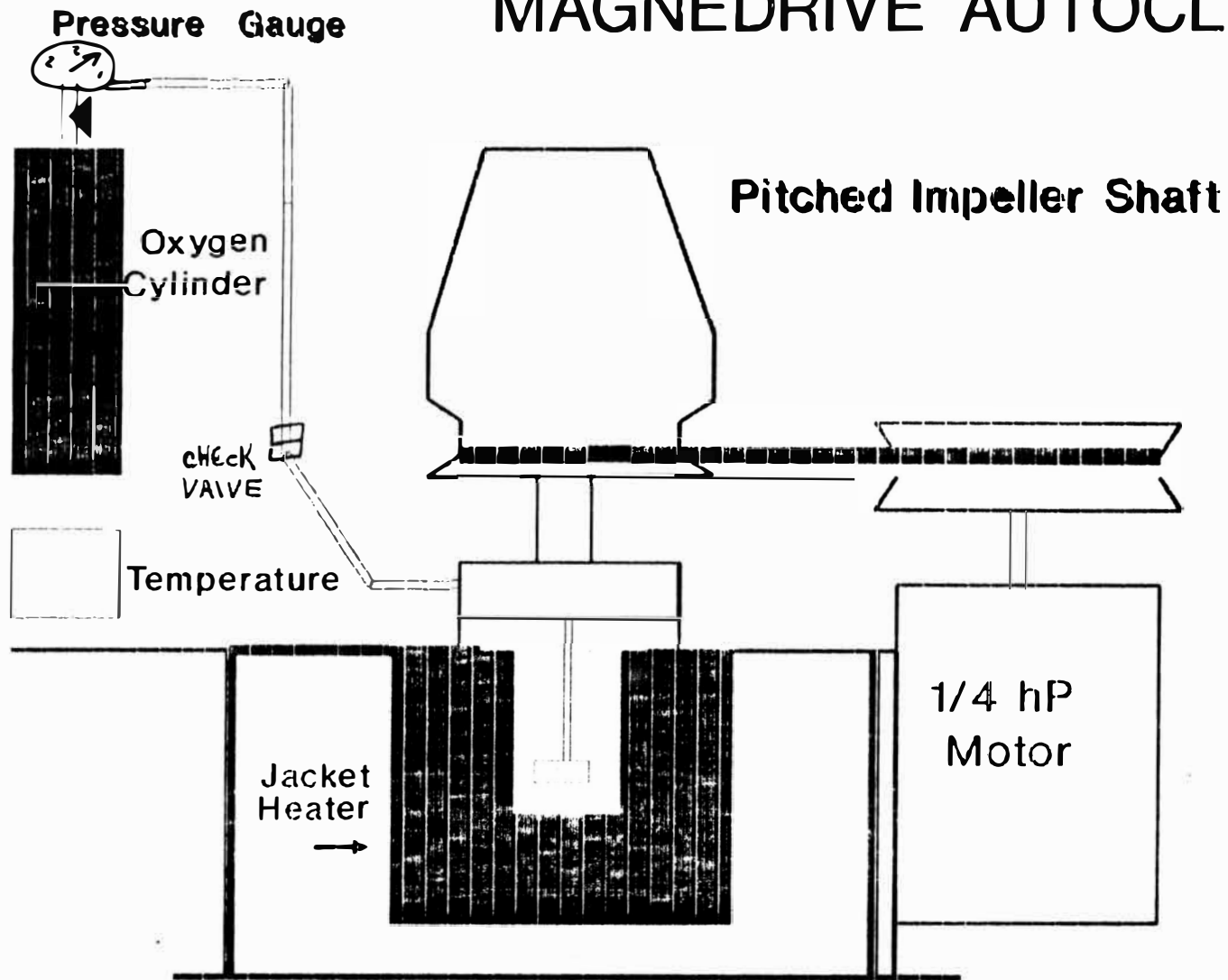


FIGURE 3.0 Magnedrive II Autoclave

to avoid the heavy metal ions present in the Kalamazoo water system. This pulp was then pre-washed with warm distilled water to remove any extractives, etc that may remain from digestion and lap pulp forming processes. This pulp was prepared for the following experimental stage.

STAGE 3: CONSISTENCY DETERMINATION

With the temperature and pressure checks of the system complete it was time to determine the highest possible consistency that provided circulation. The sample vessel circumference of 1-7/8 inches and depth of 7-1/2 inches placed severe limitation on achievable consistency ranges. Industrial oxygen delignification is performed at medium and high consistency for the most part with a few mills working at low consistency.

By laboratory limitation this experiment is limited to low consistency delignification. A clear, plastic graduated cylinder modified to meet the dimensions of the sample vessel was mounted adjacent to the vessel as shown in FIGURE 4.0. The clear cylinder enabled observation of actual fiber circulation. The highest achievable consistency that still assured strong fiber circulation was 4.0 percent. To achieve this high of consistency the flat paddle-wheel impeller was replaced with a 45° pitched impeller. (See FIGURE 5.0)

CONSISTENCY DETERMINATION APPARATUS

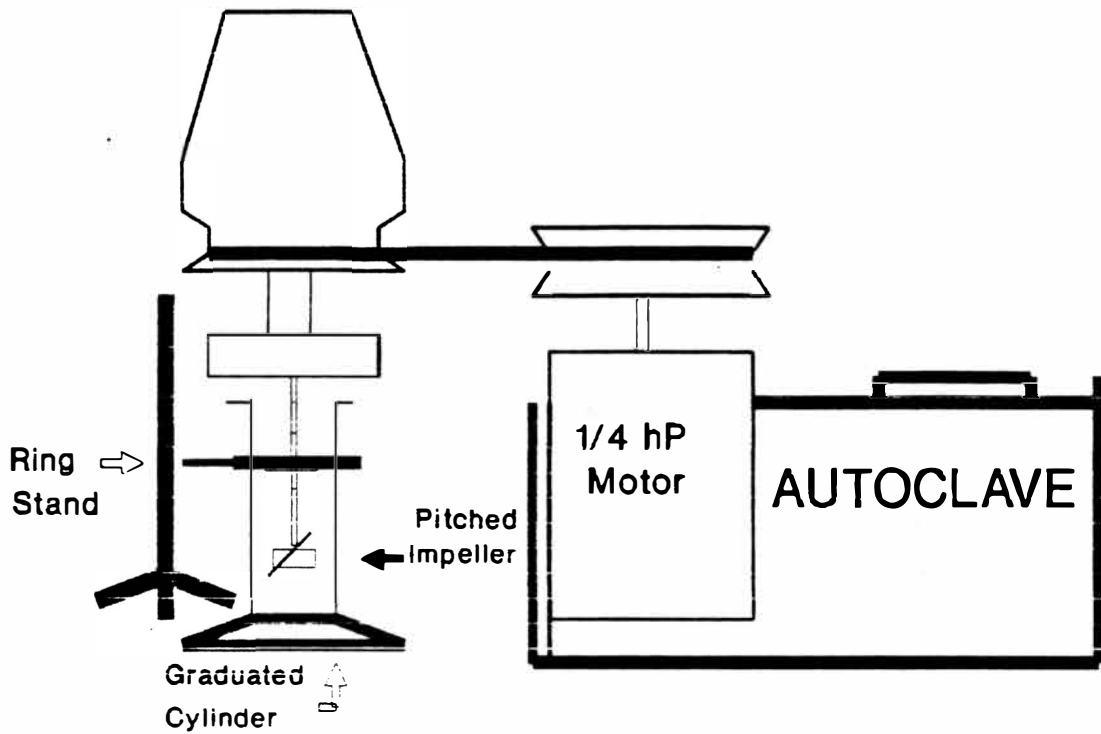
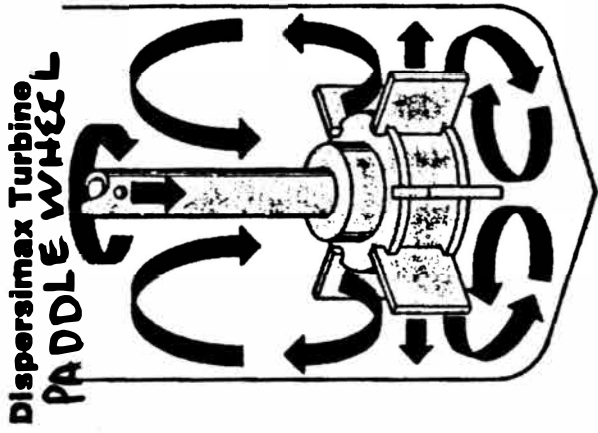


FIGURE 4.0 Consistency Determination Apparatus



Pitched Blade Turbine

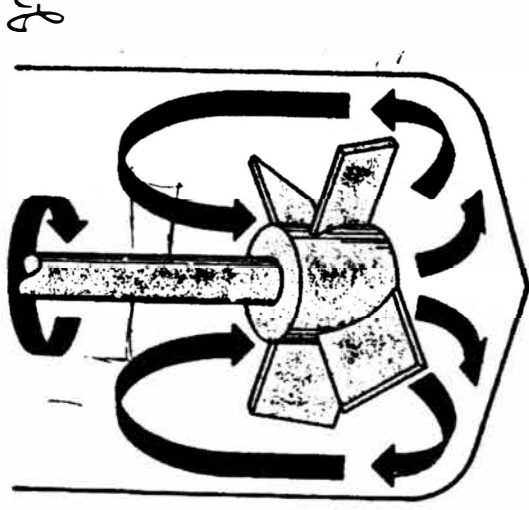


FIGURE 5.0: PADDLE vs. Pitched Impeller

STAGE 4: RETENTION TIME DETERMINATION

As stated in the Literature Review, approximately 50 percent of the lignin can effectively be removed from a conventional kraft pulp. More extensive delignification results in the degradation of pulp carbohydrates, when carbohydrate protectors are not used. The "Klason Insoluble Lignin" test was used to determine the experimental retention time. Note respective TAPPI STANDARD PROCEDURES were followed for this test. Two "Klason Insoluble Lignin" test were performed upon the untreated base stock to determine the original insoluble lignin content of the pulp.

Then oxygen delignification was performed at retention times of 30 and 45 minutes. The experimental constants of TABLE 1.0 were maintained throughout the delignification process. Base stock without the addition of carbohydrate protectors were used for this portion of the experiment. At a retention time of 45 minutes it was found that 48 percent of the original "Klason Insoluble Lignin" had been removed by the process of oxygen delignification. As a result of the long duration (6+ hours per test) of the "Klason Lignin" test an important assumption was made. KEY ASSUMPTION for the remainder of the experiment, it was assumed that a retention time of 45 minutes consistently produced a delignification of approximately 48~50 percent. It is important to note that this assumption of 45 minutes retention time is supported by actual "Klason Lignin Test" performed upon the base stock without the addition of protectors. The line graph in FIGURE 6.0 visually demonstrates the above statement.

Determination of Retention Time (50 % Original Insoluble Lignin)

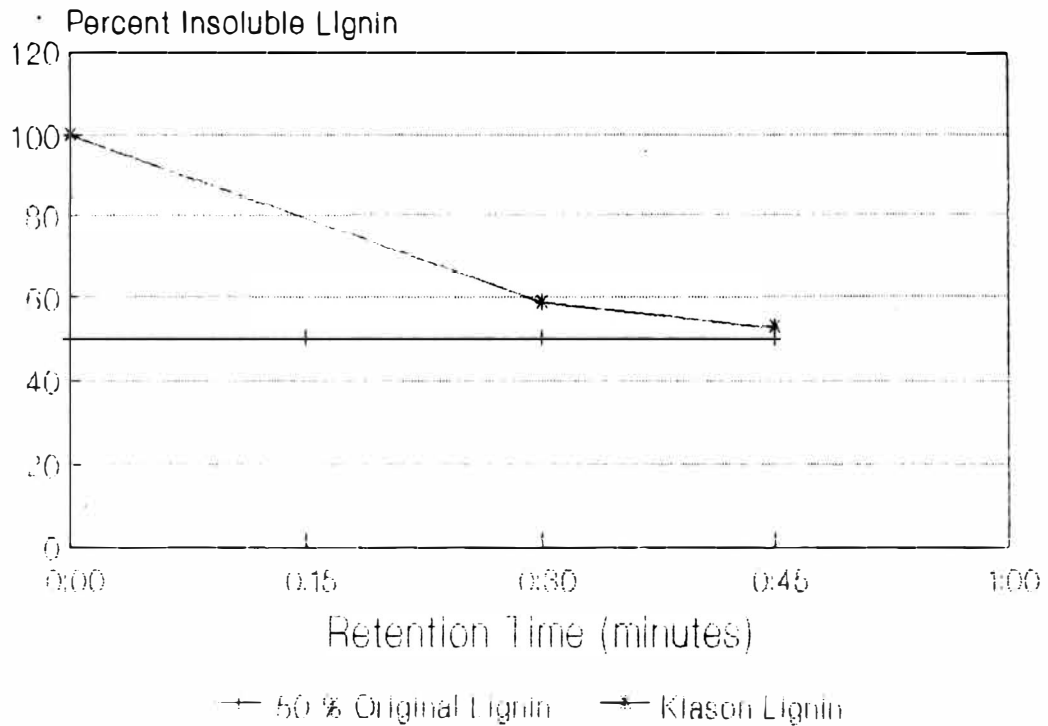


FIGURE 6.0 Retention Time Determination

STAGE 5: STOCK PREPARATION

During this stage the pulp to be used for the experiment was prepared following the procedures specified in STAGE 2. This same batch of pulp was used for all specimen runs. This was done in order to avoid variations in stock preparations that may alter test results.

Chemical preparation took place during this stage, with all chemicals found in useful form in the WMU's, Paper Pilot Plant stockroom. Chemical additions were prepared of the protectors to make concentrations of 0.5 percent on oven dry weight of pulp in the test specimen. Caustic Soda (NaOH) was added to maintain the pH at 10. Both the pH and the chemical concentrations are within ranges cited by articles read for the Literature Review.

STAGE 6: OXYGEN DELIGNIFICATION

During this stage the prepared specimen was placed and sealed into the vessel. The experiment was then underway. When the temperature reached 120°C, oxygen was used to flush relief vapors three times. After the third release of vapors a partial pressure of 120 PSI was maintained by constant addition when required. After the 45 minutes of retention time the vapor was released and the pulp removed.

The now delignified pulp was dilution washed twice with 2000ml of warm distilled water and drained through a 100 mesh screen. A fiber pad was created using a Buchner Funnel and conditioned following respective TAPPI STANDARD procedures.

STAGE 7: PULP TESTING

The effectiveness of the $Al_2(SO_4)_3$, and EDTA as carbohydrate protectors was determined using viscosity and brightness test for comparison. The intrinsic solution viscosity of a pulp measures the average degree of polymerization. Viscosity provides an indication of the degradation (decrease in molecular weight) resulting from the delignification process. The pulp viscosity is sharply decreased when the pulp is delignified with oxygen and alkali without the presence of degradation inhibitors. TAPPI STANDARD procedures were followed directly for the execution of these tests. Two viscosities were taken for each run. Each run was duplicated to assure consistency in results.

RESULTS AND STANDARD VALUES:

This section contains graphs corresponding to the experimental design and procedure. Figure 6.0, as viewed earlier, is a representation of the " Klason Insoluble Lignin ". Figure 7.0 is a graphical representation of viscosity test comparing results of all trials. Figure 8.0 visually compares the brightness test results for each group. FIGURES 9.0 - 18.0 representing actual test values and graphs corresponding the individual agents can be found in Appendix I. Table 2.0 and 3.0 provide average values and standard deviations of actual test results.

TABLE 1.0: Experimental Constants

EXPERIMENTAL CONSTANT	VALUE
CONSISTENCY	4.0 %
OXYGEN PARTIAL PRESSURE	120 psi
TEMPERATURE	120 ° Celcius
RETENTION TIME	45 minutes
pH	10

TABLE 2.0: Average Viscosity Values

SAMPLE	AVERAGE TEST VALUES	STANDARD DEVIATION	STANDARD VARIANCE
BASE (no inhibitor)	24.5	1.3	1.2
BASE (45 minutes)	---	---	---
MAGNESIUM SULFATE	19.1	1.0	1.0
ALUMINUM SULFATE	25.1	1.1	1.2
ETHYLENEDIAMINE TETRA ACETIC ACID	21.2	0.8	0.6

TABLE 3.0: Average Brightness Values

SAMPLE	AVERAGE TEST VALUES	STANDARD DEVIATION	STANDARD VARIANCE
BASE (no inhibitor)	23.9	0.73	0.53
BASE (45 minutes)	27.0	0.72	0.55
MAGNESIUM SULFATE	26.6	0.41	0.17
ALUMINUM SULFATE	25.1	0.49	0.26
ETHYLENEDIAMINE TETRA ACETIC ACID	25.5	0.74	0.53

Viscosity Comparison (Protectors at 0.5 % on Oven Dry Pulp)

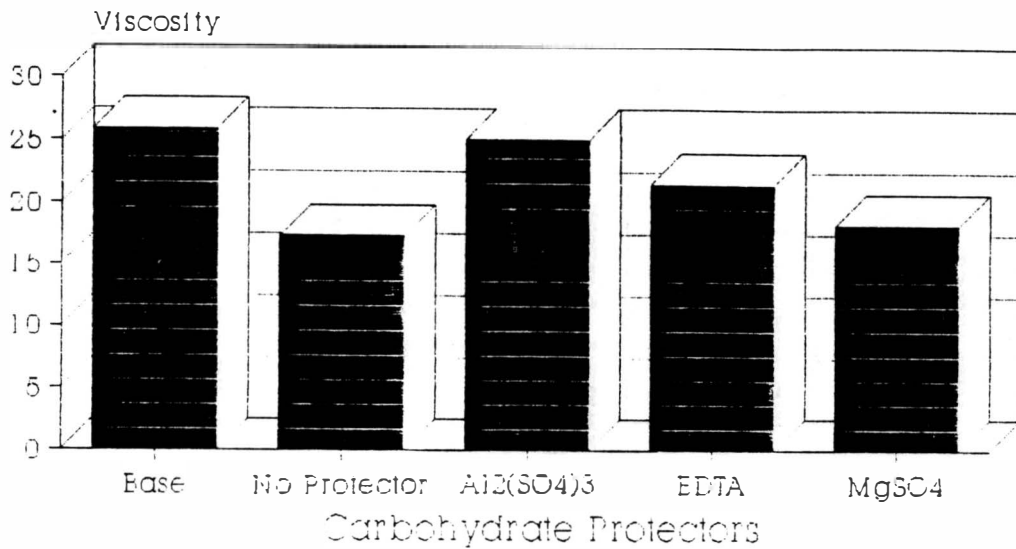


FIGURE 7.0 Viscosity Comparison

Viscosity Comparison (Protectors at 0.5 % on Oven Dry Pulp)

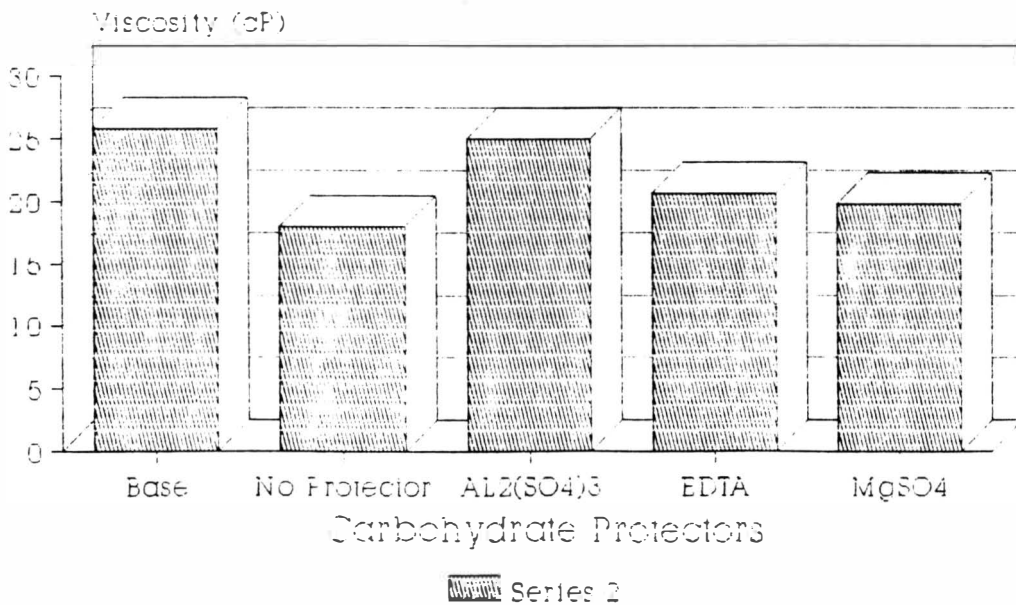


FIGURE 8.0 Viscosity of Base (no protector)

Comparison of Average Brightness (45 minutes, except for BASE)

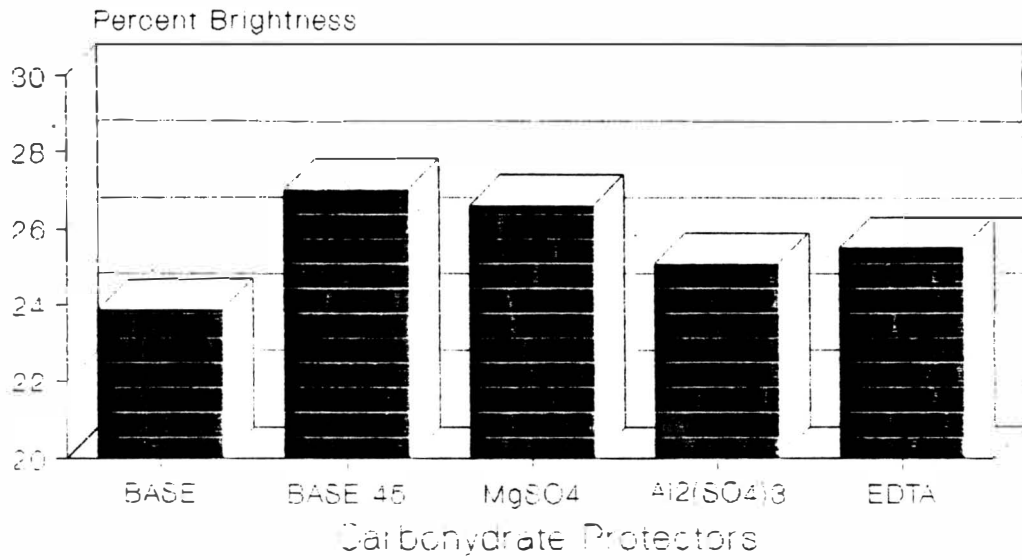


FIGURE 9.0 Brightness Comparison

DISCUSSION OF RESULTS:

The following discussion will analyze the results of this oxygen delignification experiment. To best explain the results without much confusion, one testing result will be discussed at a time. FIGURE 6.0 displays the results of the Klason lignin test used to determine the retention time. The object here was to determine the retention time that would provide fifty percent lignin removal from the pulp. As the graph demonstrates the above retention time was found to be 45 minutes. This time was therefore used for the remainder of the experiment as explained in STAGE 4 of the experimental procedure.

FIGURE 7.0 shows a graphical representation of the viscosity test results. This graph allows a visual comparison between the three different protectors to be made. By observing the graph, one can see that aluminum sulfate and ethylenediamine tetraacetic acid do act as effective carbohydrate protectors. The above statement holds for this experiment as both $Al_2(SO_4)_3$ and EDTA demonstrate viscosities higher than that provided by magnesium sulfate. Again magnesium sulfate is accepted by industry as a carbohydrate protector. Since degradation is indicated by a decrease in viscosity the higher the viscosity the better the protection.

This raises an interesting question if the two agents perform so well as protectors why are they not more frequently used? This can impart be explained by looking at economics. EDTA is much more expensive than $MgSO_4$ and $Al_2(SO_4)_3$. Therefore its benefits as a protector may not outweigh its cost. Now aluminum sulfate is the

less expensive of three, however, its use is limited by effect on the system. In abundance the presence of aluminum sulfate may create difficulty in further plant operations. FIGURES 9-13 provide comparison for trials within a protector group. These figures can be found APPENDIX I. No significant variation is observed in these values, thereby increase the validity of the testing results.

The graph in FIGURE 7.0 represents a comparison of the average brightness values for the individual agents. As the presence of lignin influences the pulp brightness, an increase in brightness can be attributed to the delignification of the pulp. Observing this graph, one can see a brightness increase for all trials after a retention of 45 minutes. This supports the earlier assumption that delignification is taking place. FIGURES 14 - 18, found in APPENDIX I, provide comparison of the values within a protector group. These graphs demonstrate insignificant variation between test results, thus an indication of uniform delignification.

CONCLUSION

This thesis was a success in that it determined that both Aluminum Sulfate and Ethylenediamine-tetraacetic acid provided ample carbohydrate protection as compared to magnesium sulfate when used during oxygen delignification. Through execution of this experiment the following points were confirmed: Carbohydrates degradation occurs during oxygen delignification resulting in a decrease in pulp quality. Intrinsic viscosity provides an indication of pulp degradation. The viscosity of the pulp is sharply decreased when pulp is delignified with an oxygen and alkali process.

Carbohydrates are attacked by the decomposition of hydroperoxides. This reaction is catalyzed by the presence of heavy metal ion, free radicals. Carbohydrate protectors function by deactivating the heavy metal ions, thereby reducing the rate of attack on the carbohydrates. The brightness test results confirmed the presence of delignification. This experiment developed a relatively indepth understanding of the oxygen delignification process.

SOURCES OF EXPERIMENTAL ERROR:

Experimental error may be responsible for some of the variation observed in the test results. As a result of coarse temperature control the heating control may have varied from run to run. The small vessel volume, as well as its limited accessibility reduce the amount of stock available. With larger stock samples, factors slightly influencing the results may not have been recognizable. Error in test results may have been a result of poor procedural execution or failure to clean viscosity tubes perfectly. The unavailability of proper laboratory equipment made the execution of this experiment complex and cumbersome.

RECOMMENDATIONS:

Three key recommendations are pointed out below. The protectors examined in this thesis do not perform the same at the same concentration. Therefore a study to discover the optimum addition concentrations should be performed. This study should take into account economics and post-delignification influence of the given agent on the system.

If time is available one may find it valuable to perform Klason Lignin tests on the pulp sample of each run to assure equal delignification for the study. Duplicate samples could be combined to allow testing of physical strength properties. Strength properties will provide further indication as to the effectiveness of carbohydrate protectors.

It may be of value to devise a method to determine the oxygen

consumption of the pulp. This may involve monitoring the amount of incoming oxygen. Followed by analysis of relief vapor for oxygen content.

APPENDIX I
RAW DATA AND GRAPHICAL
REPRESENTATIONS OF TEST RESULTS

TABLE 4.0: Uncorrected Viscosity Values

SAMPLE	BASE 45 MINUTES (cP)	MgSO ₄ (cP)	MgSO ₄ (cP)	Al ₂ (SO ₄) ₃ (cP)	Al ₂ (SO ₄) ₃ (cP)
A1	339.1	234.8	258.7	342.6	331.5
A2	338.1	235.0	258.6	342.7	334.6
B1	258.1	214.9	227.8	267.9	273.9
B2	257.7	215.0	227.5	267.7	272.4

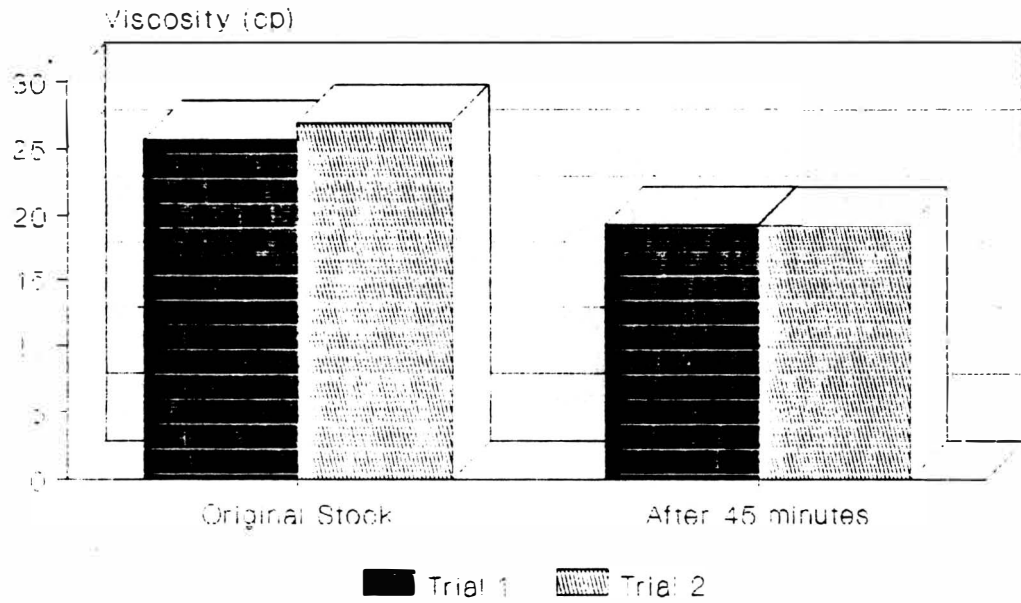
SAMPLE	EDTA	EDTA
A1	274.0	261.3
A2	274.2	260.9
B1	250.7	243.2
B2	250.9	242.9

TABLE 5.0: Corrected Viscosity Values

SAMPLE	BASE 45 MINUTES (cP)	MgSO ₄	MgSO ₄	Al ₂ (SO ₄) ₃	Al ₂ (SO ₄) ₃
A1	25.9	17.6	19.5	26.1	25.3
A2	25.8	17.6	19.5	26.1	25.5
B1	23.2	19.1	20.4	24.1	24.7
B2	23.2	19.1	20.3	24.1	24.6

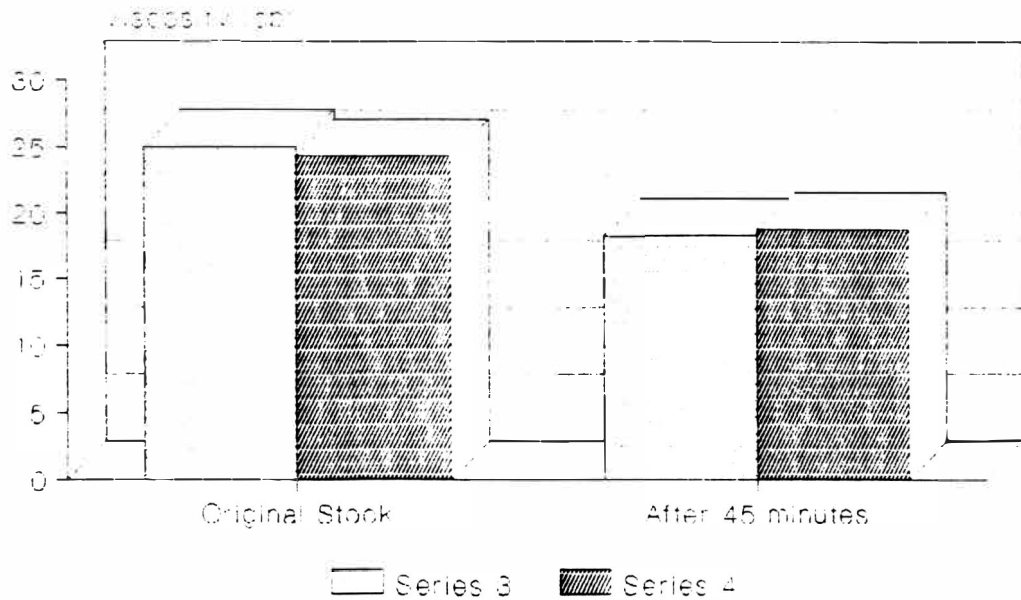
SAMPLE	EDTA	EDTA
A1	20.7	19.7
A2	20.7	19.6
B1	22.5	21.8
B2	22.5	21.8

Viscosity of Base Stock (No protector)



A.

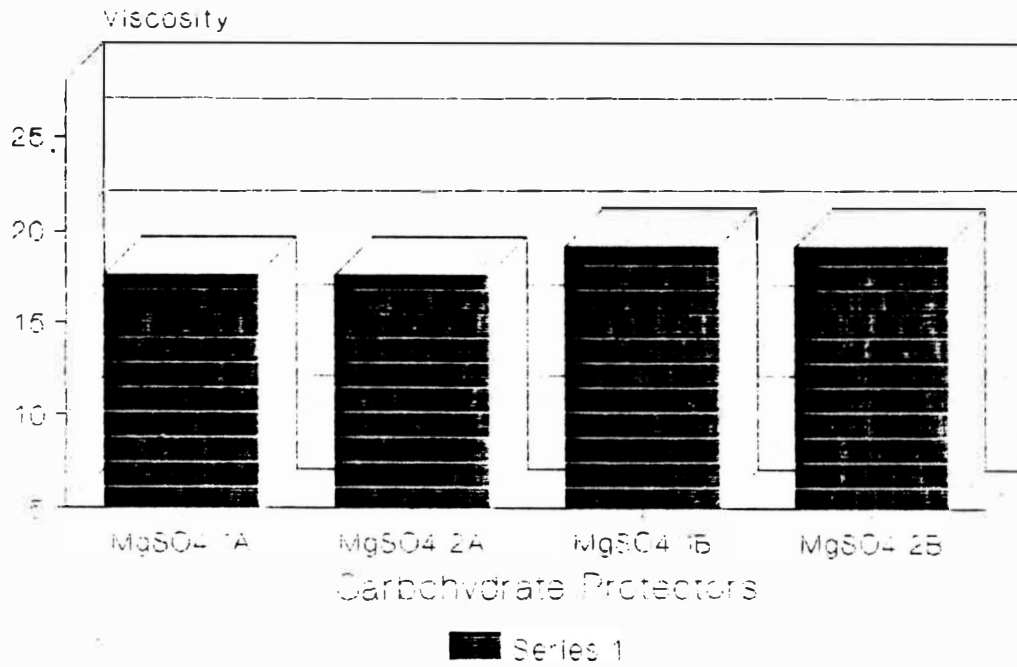
Viscosity of Base Stock (No protector)



B

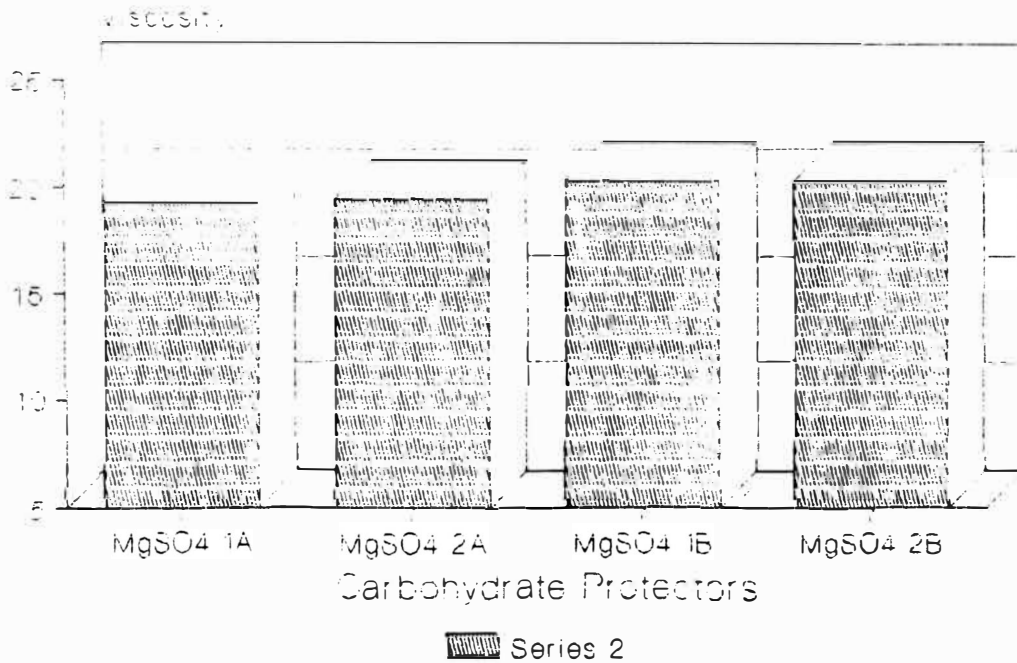
FIGURE 10.0 Viscosity of Base (45 minutes)

MgSO4 Comparison Viscosity



A

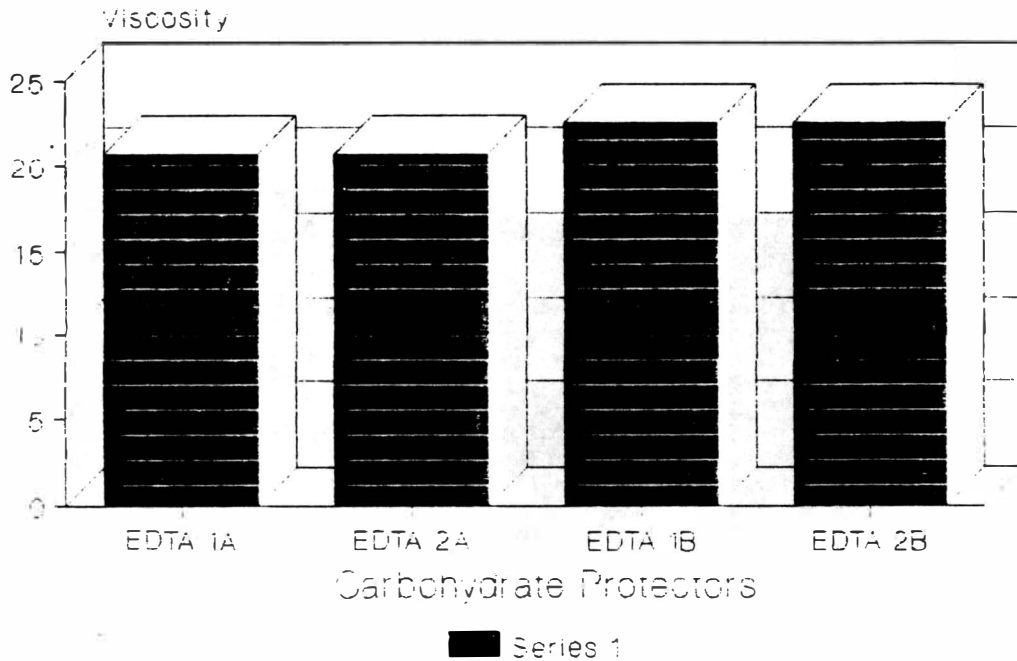
MgSO4 Comparison Viscosity



B

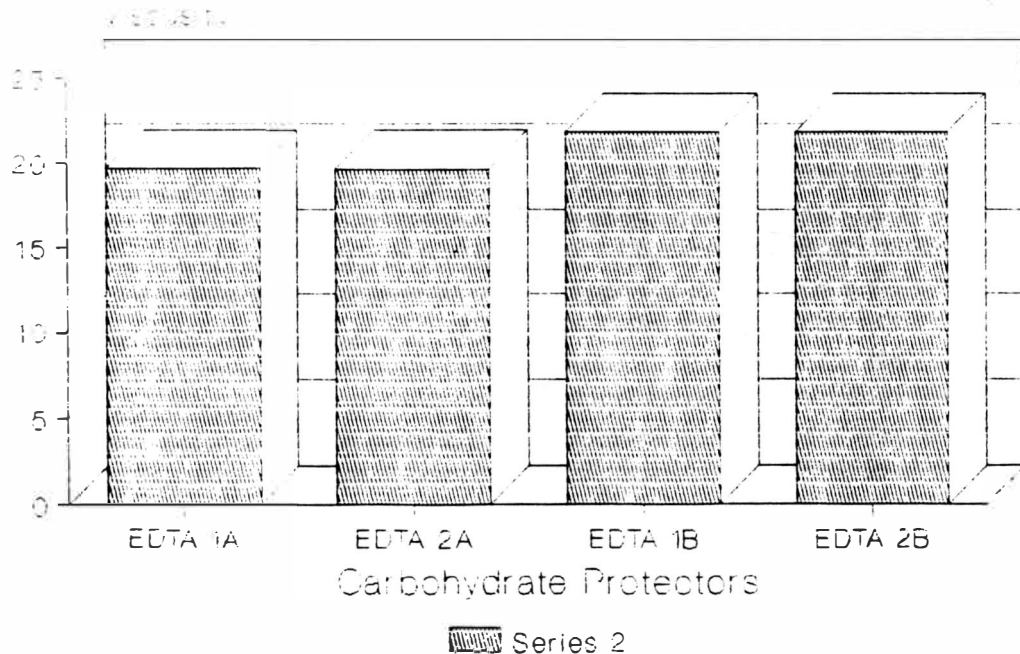
FIGURE 11.0 Viscosity of Magnesium Sulfate

EDTA Viscosity Comparison



A

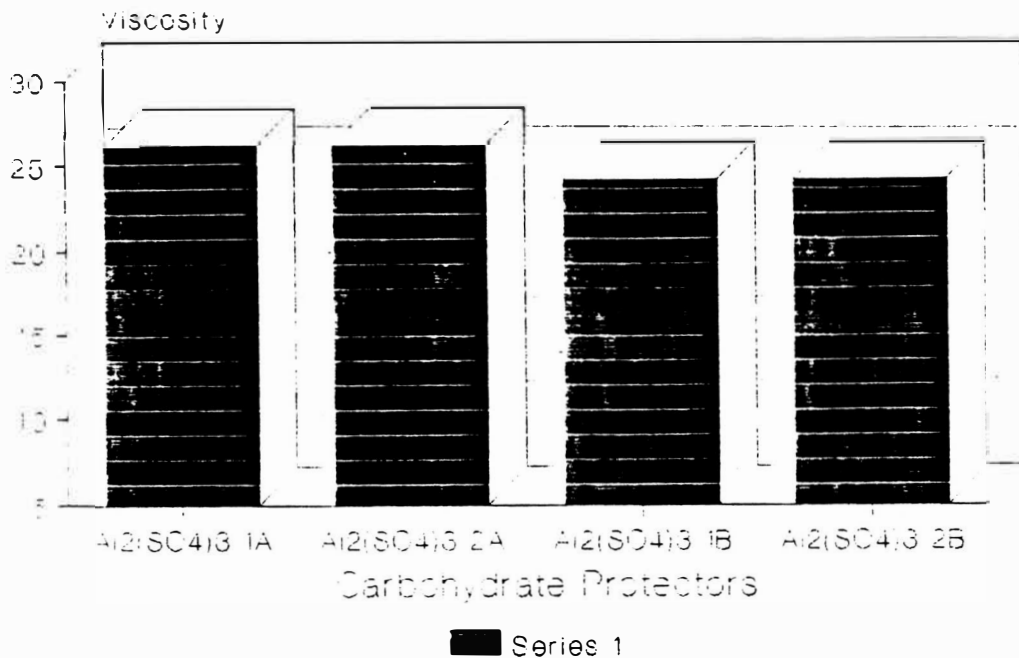
EDTA Viscosity Comparison



B

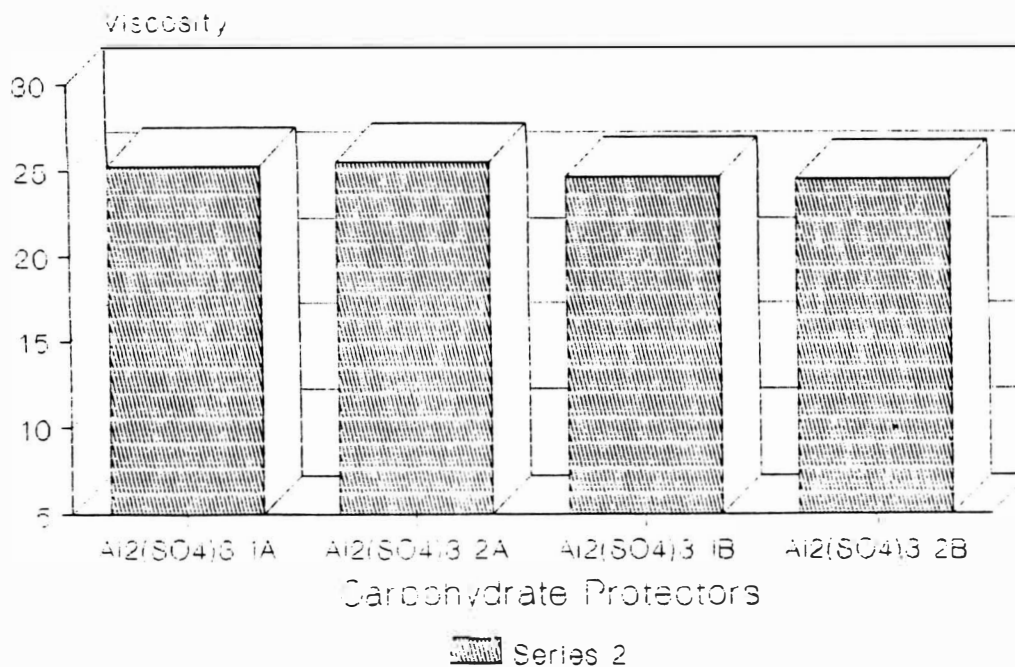
FIGURE 12.0 Viscosity of Ethylenediamine Tetraacetic acid

Al₂(SO₄)₃ Comparison Viscosity



A

Al₂(SO₄)₃ Comparison Viscosit



B

FIGURE 13.0 Viscosity of Aluminum Sulfate

TABLE 6.0: BRIGHTNESS RAW TEST VALUES

SAMPLE	RUN A	RUN B	RUN C	RUN D
BASE	25.9	23.2	23.4	22.6
	25.2	24.0	22.2	24.0
	24.7	23.7	24.5	22.1
	25.4	24.1	24.6	22.3
	24.8	23.7	25.8	24.2
	24.3	22.1	23.3	23.1
	25.4	22.6	24.7	22.3
	24.1	24.1	24.7	23.0
	24.3	24.1	24.8	23.3
	24.1	23.1	23.9	23.6

TABLE 7.0: BRIGHTNESS RAW TEST VALUES

SAMPLE	RUN A	RUN B	RUN C
BASE 45	27.0	28.5	26.2
	25.9	27.6	25.9
	26.0	28.3	25.3
	26.2	28.6	27.8
	28.2	27.9	26.3
	26.6	27.5	26.1
	27.8	28.1	27.2
	25.4	27.2	26.2
	26.0	27.4	28.1
	26.1	27.7	27.3

TABLE 8.0: BRIGHTNESS RAW TEST VALUES

SAMPLE	RUN A	RUN B	RUN C
MgSO ₄	26.6	26.0	27.3
	27.3	25.7	27.0
	26.5	26.7	25.8
	26.9	26.3	26.9
	26.7	27.0	26.7
	26.7	25.9	27.4
	26.6	25.8	25.9
	27.4	26.2	27.2
	26.7	26.7	26.7
	26.9	26.4	26.5

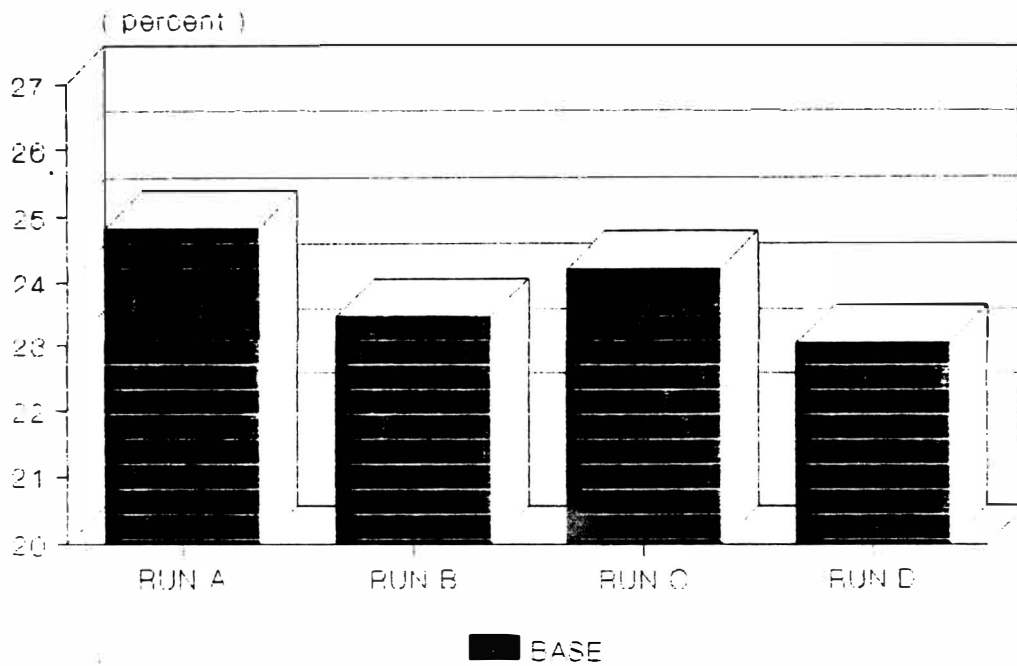
TABLE 9.0: BRIGHTNESS RAW TEST VALUES

SAMPLE	RUN A	RUN B	RUN C
Al ₂ (SO ₄) ₃	25.8	24.9	24.4
	26.8	25.3	23.9
	24.7	24.7	24.9
	25.5	25.3	24.4
	24.4	25.5	23.8
	25.8	25.4	24.6
	25.5	26.2	23.9
	26.2	25.8	24.2
	25.4	25.4	24.3
	25.1	25.7	25.1

TABLE 10.0: BRIGHTNESS RAW TEST VALUES

SAMPLE	RUN A	RUN B	RUN C
EDTA	25.7	24.3	25.6
	24.6	26.3	24.9
	26.4	23.4	25.6
	25.8	25.8	25.3
	24.9	24.4	24.3
	25.7	24.7	25.5
	25.6	26.3	26.3
	26.8	25.8	24.7
	25.8	25.9	25.8
	25.7	26.2	25.3

Brightness BASE



Brightness BASE (45 minutes)

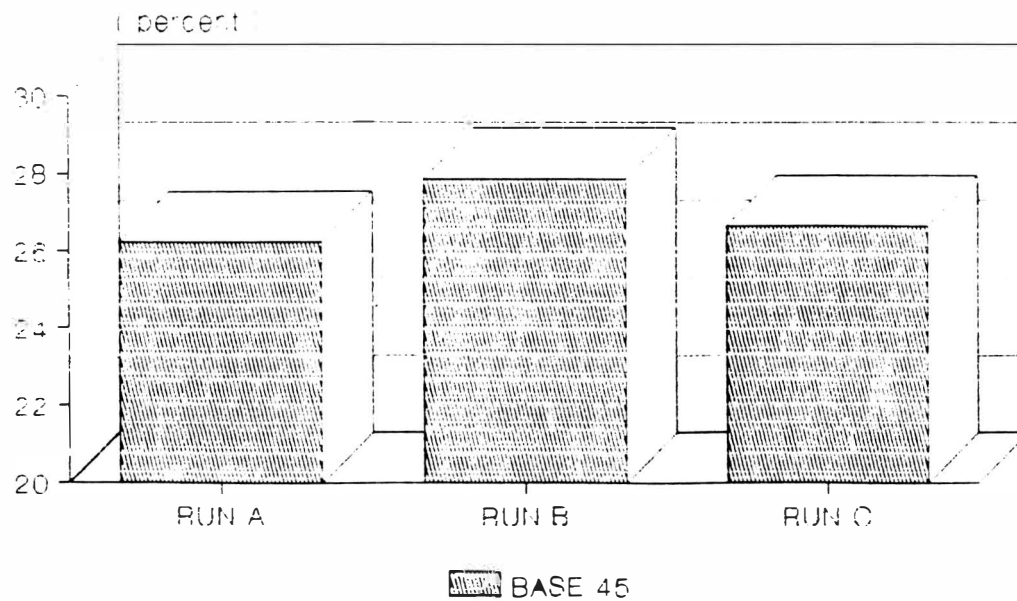


FIGURE 15.0 Brightness of Base (45 minutes)

Brightness Magnesium Sulfate (45 minutes)

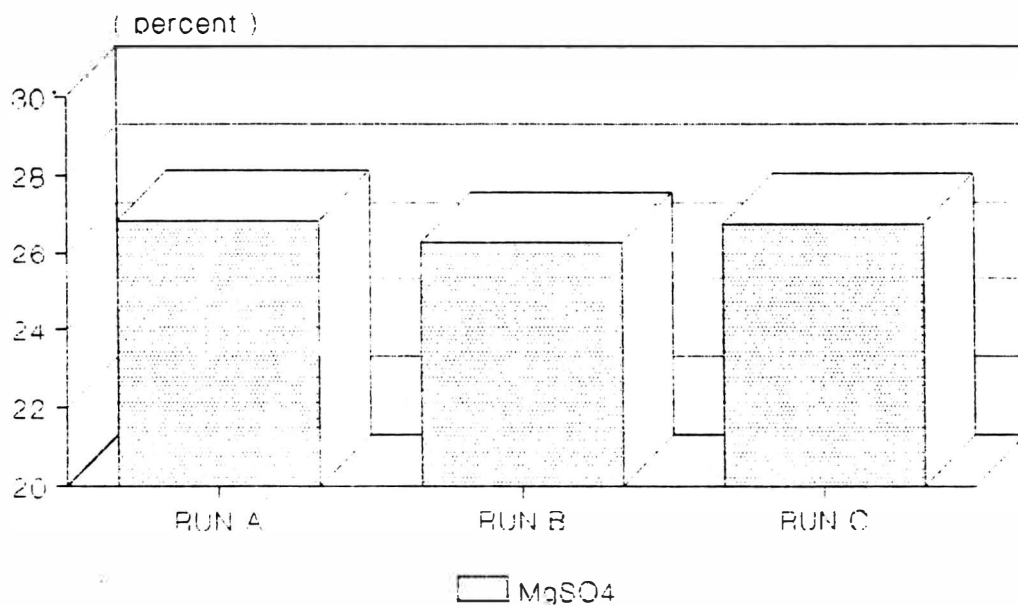


FIGURE 16.0 Brightness of Magnesium Sulfate

Brightness EDTA (45 minutes)

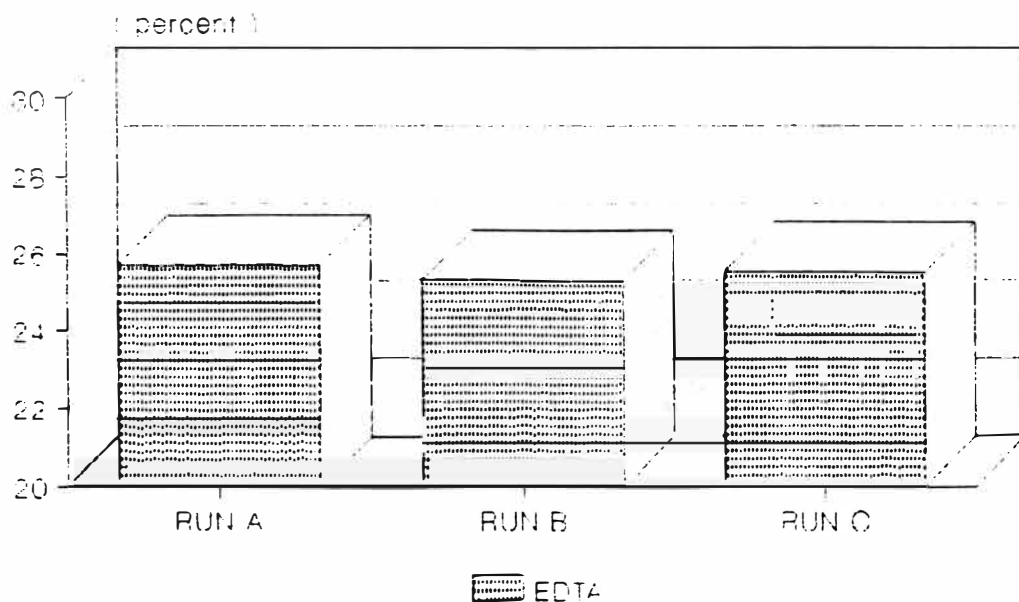


FIGURE 18.0 Brightness of Ethylenediamine Tetraacetic acid

Brightness Aluminum Sulfate (45 minutes)

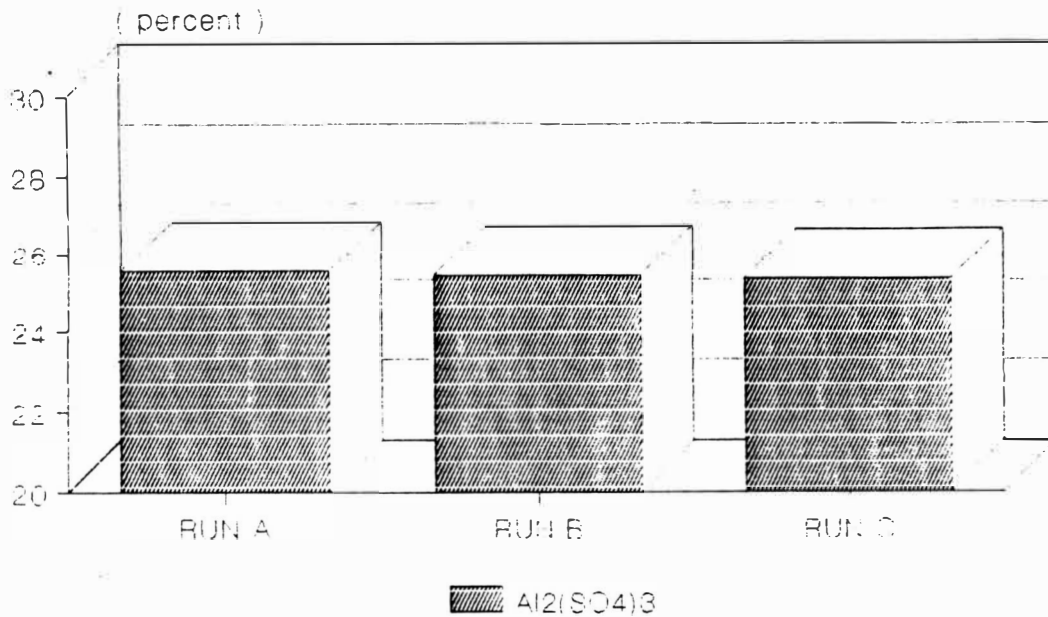
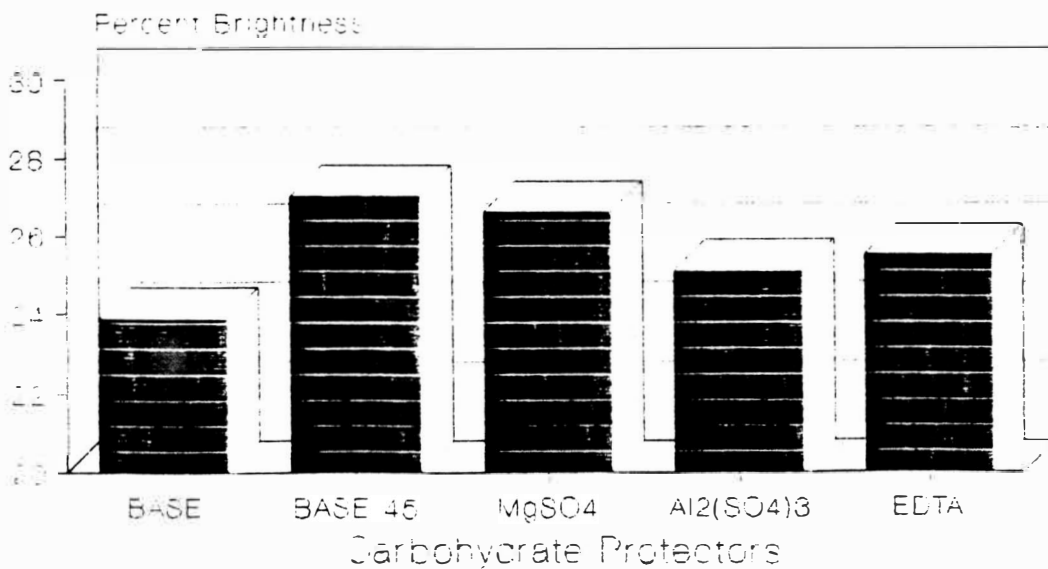


FIGURE 17.0 Brightness of Aluminum Sulfate

Comparison of Average Brightness (45 minutes, except for BASE)



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