4-1977

Surfactants as an Aid in The Kraft Pulping of Hardwood

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SURFACTANTS AS AN AID IN THE KRAFT PULPING OF HARDWOOD

by

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A Thesis Submitted To The Faculty
of the Department of Paper Science & Engineering
in partial fulfillment
of the
Degree of Bachelor of Science in Engineering

Western Michigan University
Kalamazoo, Michigan
April, 1977

ABSTRACT

Surfactants were used in the pulping of Kraft hardwood chips in an attempt to decrease cooking time while attaining the same Kappa Number. It was found that surfactants could not be used to decrease cooking time, but anthraquinone and nonlyphenol could be used to increase both yield and bond strength. Dimethylamides and quatranary ammonium salt surfactants were found to be detrimental to the pulping of hardwood, resulting in hard uncooked chips.

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HISTORICAL BACKGROUND

There have been a number of attempts in recent years to obtain benefits from the use of various surfactants in different pulping processes. Logical though such attempts may have seemed to be, the results have been less than conclusive. This raises the question of whether wetting of surfaces, interfacial tensions, and related phenomena are important factors in the penetration and pulping action of cooking liquors.

In assessing the usefullness of surfactants, it would be wise to first look at the structure of wood. All of the different cells comprising both the softwoods and hardwoods are firmly joined together by a thin common layer shared with each adjoining cell known as the middle lamella. Softening or dissolving this layer by heat and chemicals permits the cells to be seperated as they are in the pulping of wood by various processes. The flow of liquids between the tracheids of softwoods is through bordered pits, which are unthickened areas of adjacent walls spanned by a continuation of the middle lamella. The pit membranes have a central thickened and highly lignified portion known as the torus.

This is surrounded by a thinner perforated membrane with pores of a submicroscopic size. Liquids may move from tracheid to tracheid through these pores unless the torus is pushed against the cell wall opening. When it is, such pits are closed and the flow of liquids through the pores of the pit membrane is reduced or prevented.

In both the softwoods and the hardwoods there are strips of short horizontal cells known as wood rays, which extend in a radial direction. These cells act as storage depots for food substances and transport food in a horizontal direction. In addition to such distribution and movement of liquids from fiber to fiber through the pores in the pit membranes, there is what is termed a transient capillary structure existing in the cell walls when the walls are in a swollen condition. Thus, when the cell walls are swollen by water solutions of pulping chemicals, the walls are permeable and the cell wall capillaries constitute effective openings through which water solutions of relatively small molecules can move.[7]

So far, the studies that have been done are in disagreement as to penetration increases due to use of surfactants.

While these studies are in disagreement as to how the surfactant works, they all show that the use of a wetting-agent helps the pulping process. A look at surfactants shows that there are three basic types: ionic; cationic; and non-ionic. All surfactants have properties which allow them to be used as wetting agents, detergents, antifoams, foam inhibitors, etc.

To determine which type of surfactant could be used in the pulping process, a study was done to determine their stability, that is, the retention of their ability to solubilize rosin, after exposure to high temperature (150°C), high acidity (pH 2), or both. The solubilizing power of cationic compounds were not affected by high temperature, and that of anioic was slightly reduced. Solutions of sulfurous acid at pH 2 increased the solubilizing power of anionic and nonionic compounds. The simultaneous action of high temperature and low pH caused the loss of activity of the cationic agents, had no effect on the activity of nonionic agents, and increased activity of anionic agents.[4]

The rate of reaction of wood and cooking liquor depends on the concentration at the reaction interface. The higher the concentration the faster the reaction. The use of a surfactant could increase this reaction by acting as a wetting agent, which would in effect increase the concentration at the wood-cooking liquor interface.[9]

The penetration of air free wood by a liquid is defined by the Poiseulle equation:

$$\frac{\text{Volume}}{\text{Time}} = K \frac{n \cdot r^4 \cdot P}{l \cdot v}$$

Where K is a constant, n is the number of capillaries, r is the radius of the capillary, P is the pressure, l is the length, and v is the viscosity.

As we know one of the properties of a surfactant is lowering interfacial tensions, which is in a sense lowering viscosity. As can be seen by the above equation a lowering of the viscosity would increase the volume of liquid penetrated into the wood.

Capillary rise is defined by the equation:

$$h^2 = r \cdot \sigma \cdot t/2v$$

Where h is the height, r is the radius, σ is the surface tension, t is the time and v is the viscosity.

As can be seen, the lowering of the surface tension would reduce the amount of capillary rise. However, hardwood penetration is mainly through pit membranes which behave according to the Poiseulle equation.[7]

With this knowledge of how surfactants can work in the pulping process, it is still uncertain how they really do work.

Work done on the semi-chemical soda pulping of straw shows that while the use of surfactant did not improve impregnation, it did work as dispersing agent on undesirable components, mainly lignin. It also worked to increase yield 3% and decrease Kappa Number by 4 units.[6]

Further studies support this theory, that surfactants play a role during the pulping process, but not during impregnation. These studies show that the role of surfactants is one of solubilizing the lignosulfonates. The mechanism of this action appears to be peptization of colloidal particles. An additional beneficial action of these agents is the breaking of adhesion bonds binding the extractives to cellulose, also through a peptizing action.[5]

However, there have been studies done which do not agree with the previously mentioned theory. Studies concerning the impregnation of wood chips and blocks with NaOH solution, show that the rate of impregnation is influenced by fiber direction (highest in longitudinal direction and lowest in radial direction) and is increased significantly by the presence of a surface active agent. The presence of a surfactant

almost doubles the amount of caustic soda reacting with the wood and results in a more uniform delignification.[2]

According to work done by a team of Russians, there is experimental evidence for a slower absorption of water and Kraft white liquor by heartwood, and for this reason the addition of a surfactant is recommended. Black liquors from Kraft cooks of pinewood contain about 4% resin (based on total solids), which can be assumed to act as a surface active agent when saponified by the alkali of the liquor, facilitating the penetration of the liquor chemicals in the wood. Tests were carried out with tall oil, saponified tall oil, and sulfate soaps on pinewood Kraft cooks. A 10% addition of tall oil had a detrimental effect, apparently because a large portion of NaOH was used to neutralize the fatty and rosin acids. Saponified tall oil reduced the amount of undercook and increased the yield of screened pulp 5%. A similar effect was seen with the addition of 5% sulfate soap. Further studies showed that the 5% addition of soap improved the liquor penetration only for the first two hours of impregnation.[4]

Work done by Buckman Laboratories with dimethylamides of long-chain, unsaturated fatty acids in the

penetration can be improved. These compounds are all surfactants in the sense that the molecules concentrate and orient at interfaces. The dimethylamides thus may increase the amount of cooking liquor through the opeinings in the pit membranes by facilitating wetting of the walls of these capillaries by dissolving resinous materials from partially or completely plugged cappillaries, and/or dissolving resins or other materials which may have cemented the tori of aspirated bordered pits to overhanging cell walls. In alkaline cooking, however, the liquors swell wood more and thereby increase the size of the transient cappillaries in the cell walls. The relative contribution of these capillaries to the total flow of cooking liquor into wood chips thus may be increased under such conditions. In addition to potential influence on penetration, it seems probable that the dimethylamides may participate in the delignification process.[1]

One of these dimethylamides is a Buckman product, Busperse 47. The value of Busperse 47 as a pulping aid for addition to digesters derives from its penetrating and dispersing properties. The product has a relatively low affinity for the hydrophilic surface of cellulose and thus is preferentially adsorbed at resinified or lignified surfaces in the wood chips.

As the cooking liquor containing Busperse 47 reacts with the lignin binding the fibers into the wood structure, the Busperse 47 penetrates into the wood, disperses the eroded solids, and exposes new surfaces for reaction with the cooking chemicals. The result is a faster, more efficient softening of the lignin binding the fibers together and a more rapid opening of clogged capillary pores. Consequently, there is a more efficient use of the heat and cooking chemicals, which can enable reductions in cooking times, cooking temperatures, or the amounts of active cooking chemicals needed to achieve the quality of pulp desired. Busperse 47 is a nonionic surfactant which has shown to be stable at high temperatures and low pH.[1]

Another product on the market is Triton N-100 by Rohm and Haas. Work done by Wirpsa and Libby on birch logs showed a dramatic increase of liquor penetration into the wood by use of Triton N-100. This penetration was most significant in the first 6" of the sapwood and heartwood. Further studies with this wetting agent was done with 3/4" cubes of birch. The cubes were placed in water and an aqueous solution of Triton N-100. After 4.25 hours of immersion the wood was removed and moisture contents determined. With just water, the cubes had a moisture content of 46.2%, but with .05% Triton N-100 the moisture content was 76.5%.[8]

DEFINITION OF THE PROBLEM

This study was done in an attempt to decrease cooking time in Kraft pulping of hardwood chips, by using various surfactants, while keeping Kappa Number the same. In addition to Kappa Number, the pulp from these cooks were tested for strength and compared to the control cook.

EXPERIMENTAL

All cooks were done in a small stationary batch digester with a constant liquor to wood ratio of 4 to 1. The alkalinity of the liquor was 20% as Na_2O with a 3/1 NaOH to Na_2S ratio giving a sulphidity of 15%. The digester was equipped with a circulation pump, two electric liquor heaters and a steam inlet. Unsoaked mixed hardwood chips with a 43% moisture content were used. The chips consisted mainly of oak, maple, and poplar. The cooks were two hours long at 170°C, with an average time of 1 3/4 hours to reach this temperature.

The yield of the cooks were determined by the weight of the chips coming out of the digester. The cooked chips were defibered in the laboratory Bauer Single Disk refiner at 65°C and 3% consistency. The pulp was washed and beater runs were made in a Valley Beater at 1½% consistency. Kappa Number tests were run to determine the degree of delignification. The pulp directly from the refiner was classified as to fiber length. Handsheets were made on the Noble and Wood Sheet Mold at a basis weight of 60 grams/meter^2. These handsheets were then tested for strength properties.

Several cooks were done to determine the properties of pulp produced from a standard Kraft cook. The values obtained from these cooks are shown in Table 2. The average value of these cooks are shown in Table 3 listed as control.

Cooks were then done with various surfactants. The surfactants used were, anthraquinone, dimethylamides, quaternary ammonium salts, and nonylphenol.* The surfactants were added at varying amounts based on the oven dry weight of the wood. The Kappa No. and pulp strength were compared to those obtained from the control cooks. Table 2 shows the values obtained from these cooks, with Table 3 giving the averages.

* Product names for surfactants can be found in Table 1.

RESULTS AND DISCUSSION

The long-chain unsaturated fatty acid composed of N,N-dimethylamides is a non-aqueous and nonionic liquid which is stable under both acid and alkaline conditions, even under the severe conditions of high temperature and pressure.

At a .1% addition level tests showed that this dimethylamide proved ineffective in lowering Kappa No.. It did, in fact, have no effect at all on either Kappa No. or the strength qualities of the pulp produced.

At a .5% addition level the dimethylamide proved to be detrimental to the production of pulp. This cook resulted in chips with hard centers which would not go through a refiner without continual plugging. From this information it was concluded that dimethylamides would not be suitable for use as a pulping aid to decrease cooking time.

The quaternary ammonium salt is an aqueous dispersion of stearyl dimethyl benzyl ammonium chloride at 25% solids, which is used as a softening agent for textiles, etc.

Again, as with the dimethylamide, it was found that the chips coming out of the digester had extremely hard centers at an addition level of .5% and also

at an addition level of .1%. From this it was concluded that this surfactant would not be suitable for reducing cooking time.

The nonylphenol, which was added at a .1% addition level showed increases in both yield and bonding strength of the pulp produced. It also refined as easy or easier than the control pulp. However, because this surfactant did not decrease the Kappa No. also, it would not be suitable for use as a means of decreasing cooking time. The pulp from this cook also had a tendency to foam more than the control pulp. Another cook was done with this agen to see if the results could be duplicated. As Table 2 shows, the results were duplicated.

Anthraquinone is an insoluble yellow crystalline material which has been shown to be effective in increasing yields of Kraft pulps. It was found, as would be expected from previous studies, that the anthraquinone did increase yield and also strength properties as can be seen by the graphs in the appendix. Like the nonylphenol, it did also increase Kappa No. and refined very easy. However, because of the increased Kappa number this additive does not appear to be useful as a means of decreasing cooking time.

CONCLUSIONS

As was stated earlier in this paper, ther are two ways in which liquor may get into wood chips. One way is by penetration which increases with decreasing surface tension. The other is capillary rise, which decreases with decreasing surface tension. It would appear from the Kappa No. data obtained from this project, that the action of a surfactant is more detrimental to capillary rise than it is helpful to penetration as far as the removal of lignin is concerned.

However, there is evidence that liquor penetration is increased by using surface active agents. This evidence is bond strength test which were run; namely fold, tensile, and mullen. From this data it can be seen that bond strength improved with the addition of both anthraquinone and nonylphenol. This increase in bond strength means that the lignin which bonds fibers together in wood has been better attacked and removed. This is an effect of better penetration.

TABLE I

Chemical Name	Product Name and Manufacturer
N,N-dimethylamide	Busperse 47, Buckman Laboratories
Nonylphenol	Triton N-100 Rohm and Haas
Stearyl dimethyl benzyl ammonium chloride	Triton X-400 Rohm and Haas

TABLE II

COOK	YIELD(%)	KAPPA	TEAR			TENSILE			FOLD			MULLEN		
			MINUTES OF BEATING											
			0	30	60	0	30	60	0	30	60	0	30	60
Control	52	17	75	76	57	7	8	8	87	280	430	31	43	33
Control	54	20	70	73	54	8	8	9	88	265	390	34	45	36
Dimethyl. .1%	55	20	73	75	56	7	8	8	87	272	424	33	43	35
.5%	73	38												
Q A S * .1%	73	42	Too Hard to refine											
.5%	75	43												
Nonyl.	63	25	40	44	40	7	8	10	20	510	906	20	40	38
"	64	25	44	48	40	8	10	12	17	540	1124	18	42	39
Anthra.	73	30	57	52	51	7	8	11	60	458	773	27	43	42
"	73	30	53	50	55	7	10	10	65	442	791	28	39	43

* Quaternary Ammonium Salts

TABLE III

250 Freeness

COOK	YIELD	KAPPA	CLASSIFICATION % RETAINED					TEAR	TENSILE	FOLD	MULLEN
			1		3	4	L				
Control	53	19	1.0	2.5	27.5	47.5	21.5	56	7.5	424	35
Dimethyl.	55	20	1.2	2.4	26.8	48.7	20.9	54	7.8	412	35
Nonyl.	64	25	.3	4.6	42.3	42.3	10.5	40	10.7	1064	37
Anthra.	73	30	2.0	10.0	40.0	38.0	10.0	56	11.6	885	42

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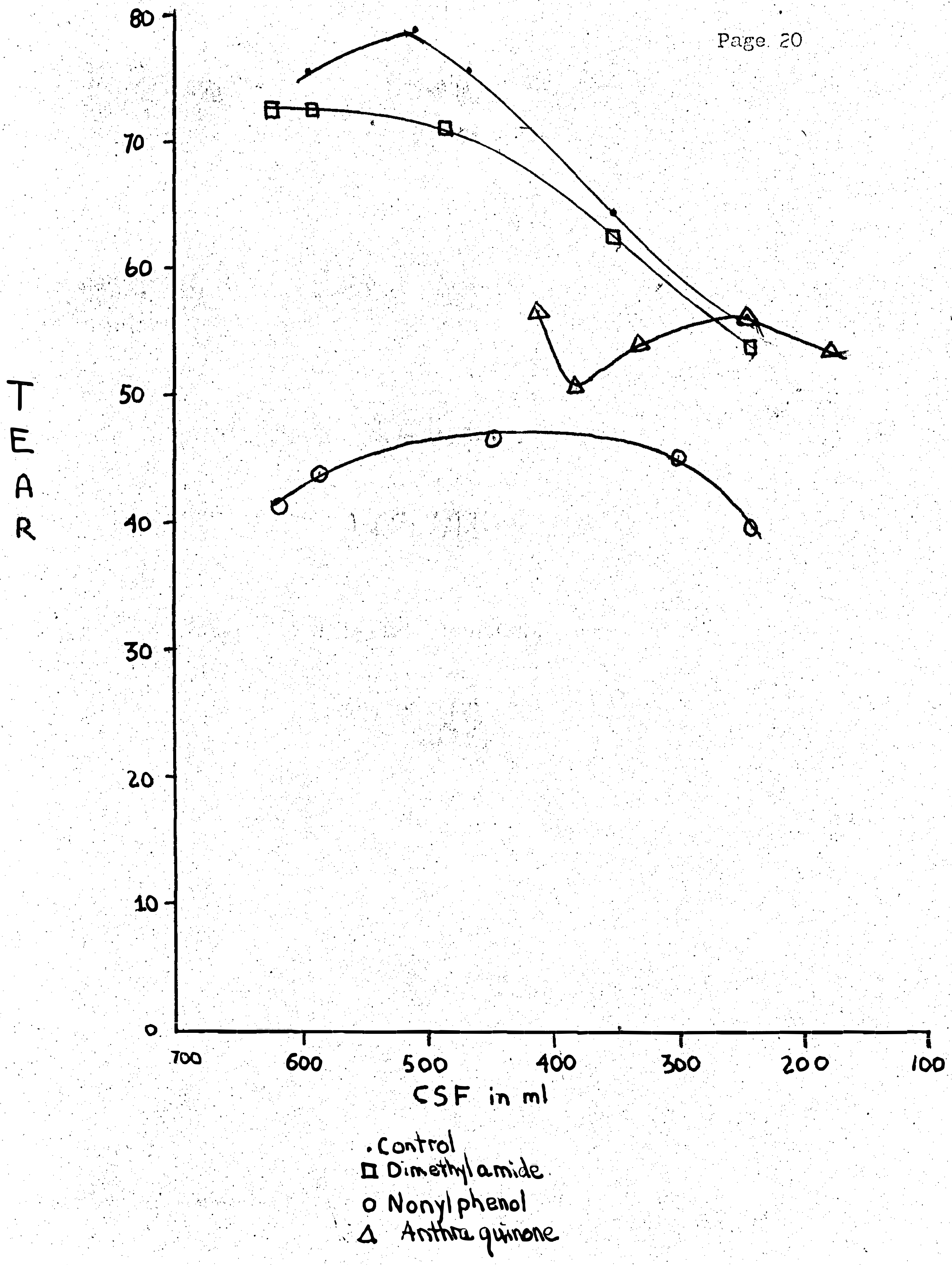
A P P E N D I X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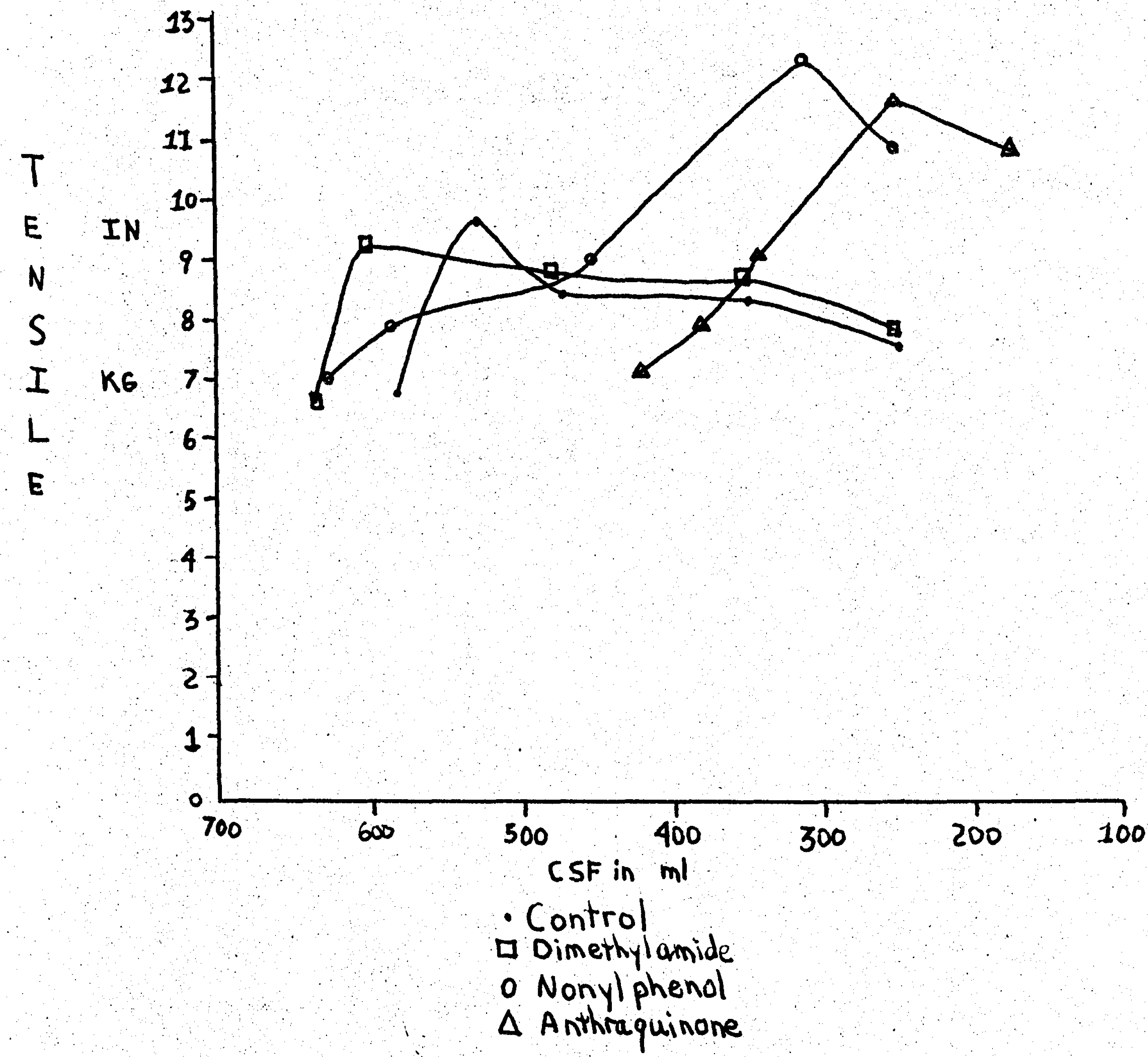
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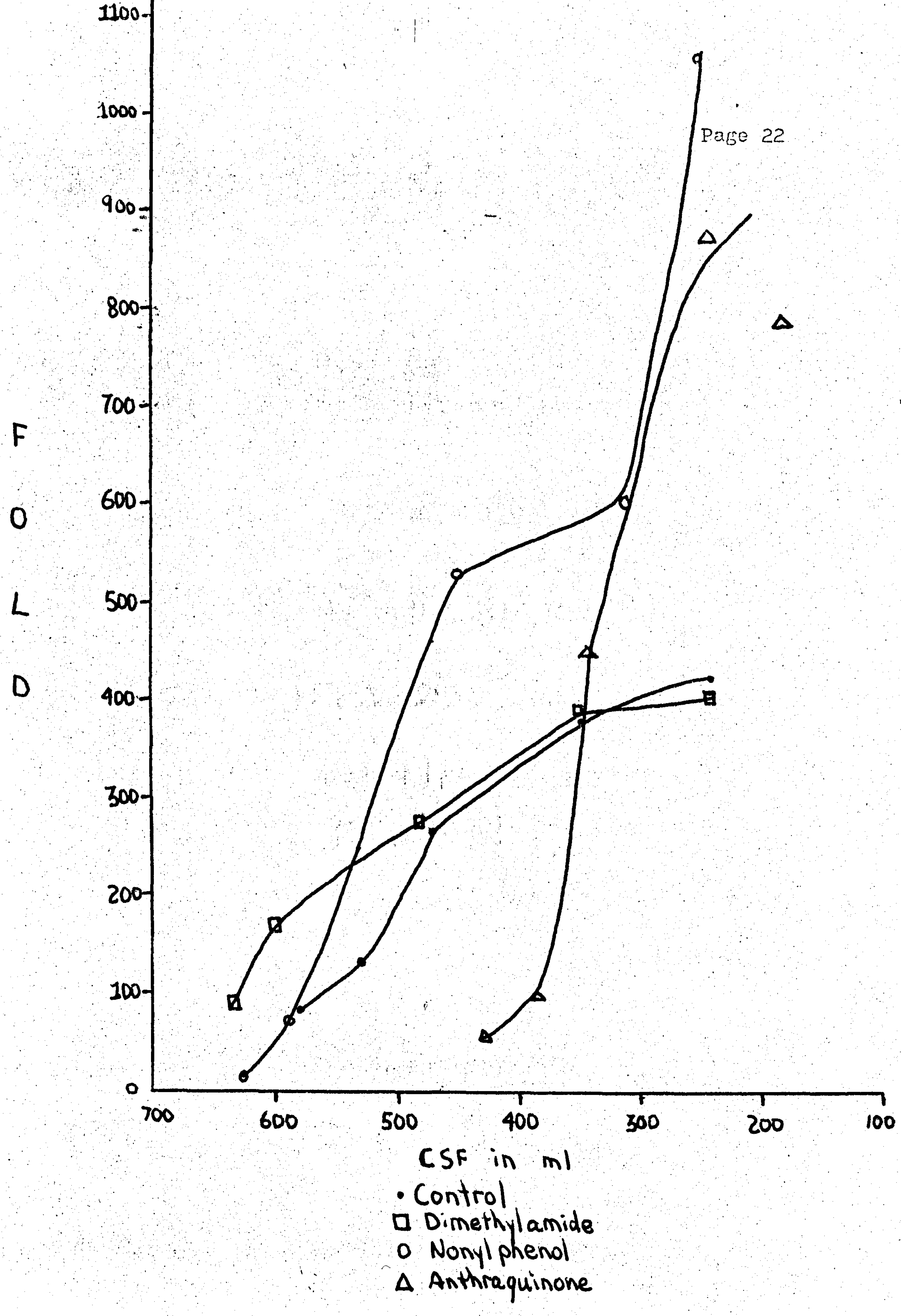
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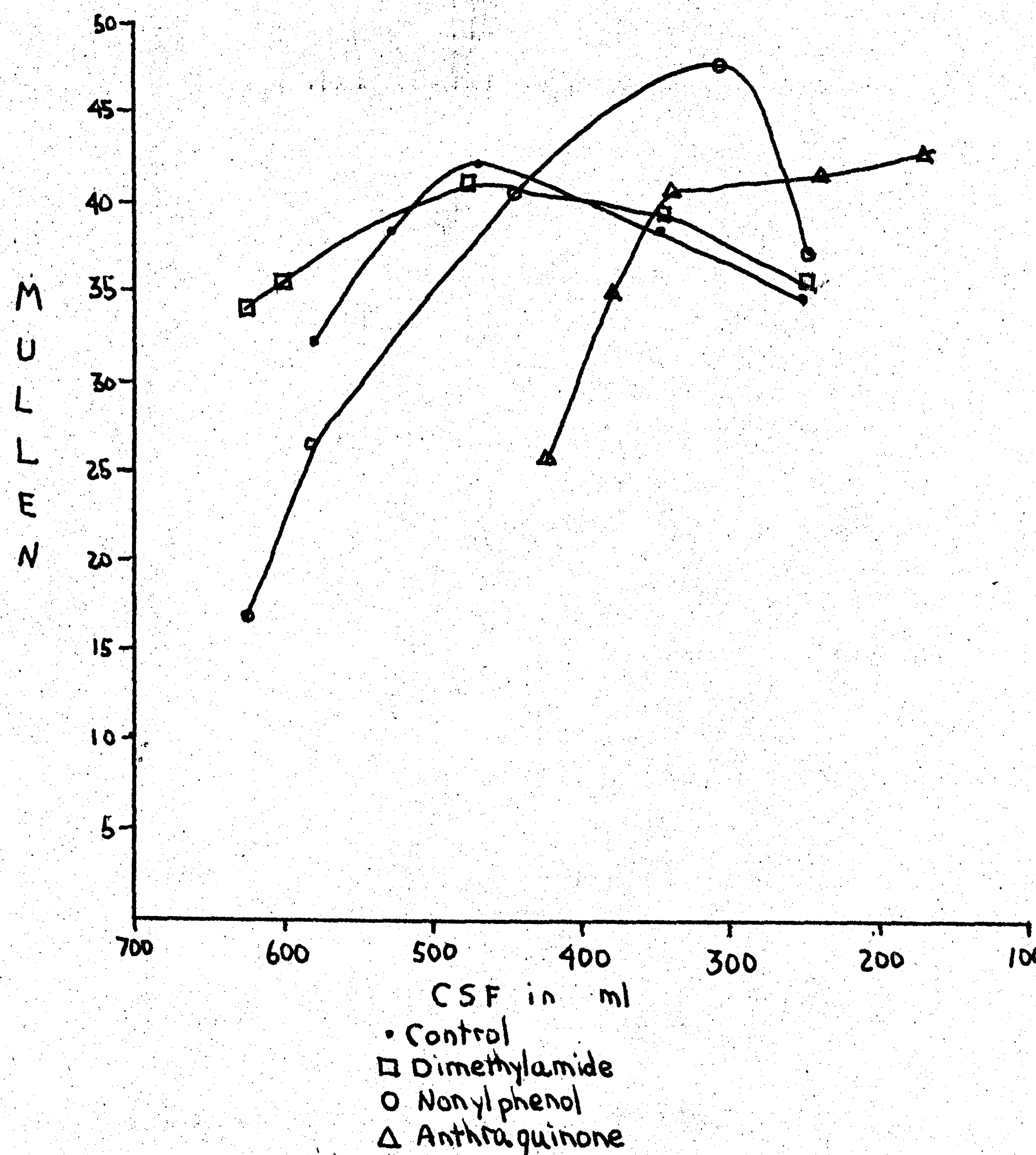
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