

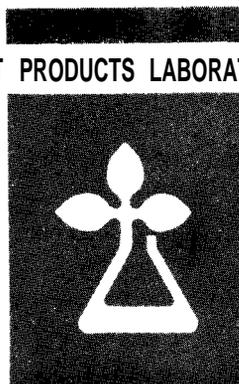
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RESEARCH NOTE

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TREATMENT OF KRAFT
PAPERBOARDS AND A
KRAFT PULP WITH
ACRYLONITRILE

Summary

Acrylonitrile ($\text{CH}_2=\text{CH}-\text{CN}$) was reacted with unbleached southern pine kraft linerboard and bleached southern pine kraft cardstock to determine the effect of this treatment on compressive strength and dimensional stability. A sweetgum kraft pulp was treated similarly before and after bleaching and the papermaking qualities of the treated pulps were evaluated.

The product qualities of these original materials changed considerably. The cardstock increased in weight by 30 percent after treatment with a 6 percent aqueous solution of acrylonitrile. However, the unbleached linerboard treated under the same conditions increased just slightly in weight.

The compressive strength of the unbleached linerboard increased 129 percent in the cross-machine direction at 90 percent relative humidity; under the same conditions the compressive strength of the bleached cardstock increased 122 percent. Dimensional stability of the cardstock increased 60 percent, but that of the unbleached linerboard was unchanged. The unbleached linerboard was, however, severely embrittled by the treatment.

Bleached sweetgum kraft pulp treated with a 6 percent aqueous solution of acrylonitrile increased in weight by 135 percent. The unbleached sweetgum kraft pulp increased in weight by only 12 percent.

The bonding capacity of the treated pulp fibers, and therefore the papermaking strength, was completely destroyed. The properties of opacity, scattering coefficient, refractive index, and moisture regain of the bleached kraft pulp were all decreased by the treatment.

TREATMENT OF KRAFT PAPERBOARDS
AND A KRAFT PULP WITH ACRYLONITRILE

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Introduction

Grafting monomers to cellulose and cellulosic derivatives is of interest because of the possibilities for producing materials with new and improved properties. Some of the improved properties of graft copolymers are decreased solubility, increased dyeability, hydrophobicity, rot and weather resistance, improved rigidity, dimensional stability, and stiffness.

Graft copolymers are formed when the monomer adds to the free radical site on the cellulose molecule. This free radical site may be produced by (a) high energy gamma radiation (8),² (b) low energy ultraviolet radiation (8), (c) redox initiation with ceric ion (4), (d) oxidation (2), and (e) chain transfer (6).

Several approaches have been taken to the problem of characterizing cellulose graft copolymers. The most common means of measuring the amount of grafted product, or percent polymer pickup, is the degree of insolubility of the copolymer in selective solvents for their respective homopolymers. Daniel and coworkers (1) extracted acrylonitrile-paper reaction products with hot dimethylsulfoxide for confirming the formation of a graft copolymer. Other selective solvents are pyridine for cellulose acetate reacted with styrene and a solution of 95 parts pyridine and 5 parts acetone for cellulose acetate--methylmethacrylate graft copolymer.

¹Maintained at Madison, Wis., in cooperation with the University of Wisconsin.

²Underlined numbers in parentheses refer to Literature Cited at the end of this note.

Another means of analyzing the cellulose graft copolymer is by complete hydrolysis of the cellulose which yields the grafted monomer in the form of a homopolymer terminated with a glucose unit. Guthrie (3), using a ceric-ion redox reaction to initiate free-radical polymerization, grafted polyvinyl chloride onto randomly labeled cellulose -C¹⁴. The reaction product was analyzed for carbohydrate content by radioactivity, chlorine analysis, infrared spectroscopy, and paper-partition chromatography. Physical sorption of labeled carbohydrate fragments was absent in the hydrolyzed graft products but the homopolymer extracted from the labeled graft copolymer exhibited a slight radioactivity. He concluded that his results are strong evidence for a primary chemical graft linkage.

According to Stannett and coworkers (7), many so-called graft copolymers actually consist of a great deal of ungrafted cellulose, a great deal of homopolymer, and only a small amount of grafted cellulose. The grafts that do exist consist of a few, very long, grafted side chains attached to the cellulose structure.

Lynch (5), using benzol peroxide as the initiator, polymerized the monomers acrylonitrile and methylmethacrylate with three different types of paper and obtained modified paper products containing from 5 to 35 percent polymer pickup. Lynch concluded that grafting of these monomers to the cellulose molecule did not occur and that paper treated with acrylonitrile is not internally polymerized.

The object of this Forest Products Laboratory study was to evaluate the effects of treating certain paperboards and a hardwood kraft pulp, before and after bleaching, with acrylonitrile. The treated material was extracted to determine the degree of actual grafting.

Materials

The material used in this study was southern pine unbleached kraft linerboard, bleached kraft cardstock used for computing machines, and bleached and unbleached sweetgum kraft pulp. The cardstock furnish consisted of 80 percent southern pine and 20 percent of sweetgum.

The chemicals used in this work included acrylonitrile, dimethylsulfoxide, (anhydrous), D-glucose, dimethylformamide, and a purified grade of ceric ammonium nitrate $\left[\text{Ce}(\text{NH}_4)_2 (\text{NO}_3)_6 \right]$

Polymerization Procedure

Paperboard

The ceric-ion redox system as employed by Daniel and coworkers (1), was used with slight modification for treating the paper products with the acrylonitrile monomer. To minimize the amount of polymerization occurring outside the paper sheets, long-fibered stock was used because there is a greater tendency for short fibers to separate from the sheet during treatment.

Six 8- by 10-inch oven-dry sheets supported in a stainless steel rack were placed in a stoneware crock and deaerated with carbon dioxide for 10 minutes. The rack and sheets were then immersed in a crock containing 19 liters of an aqueous solution of acrylonitrile monomer which had previously been flushed with carbon dioxide for 20 minutes. This system was stirred and flushed for an additional 10 minutes with carbon dioxide by means of a gas dispersion tube. A sufficient amount of a stock solution³ of 0.1 molar ceric ammonium nitrate and 1.0 molar nitric acid was added to the system to give a final concentration of 0.005 molar and 0.05 molar, respectively. The polymerization reaction was initiated upon addition of the ceric salt solution and duration of immersion, or of reaction, was measured from this moment. Duration of immersion in this study was 20 minutes. During the immersion period the system was continuously flushed with carbon dioxide. The reaction was carried out at 25°C. and at atmospheric pressure. Initial pH of the reaction medium was 2.4, and the final pH was 1.8.

The modified paper products were thoroughly washed with warm water and dried to constant weight at 105° C. in a forced-draft oven. Any weight increase was expressed as percent polymer pickup, which is equivalent to the weight of monomer grafted expressed as a percent of original weight of sample.

Percent polymer pickup =

$$\frac{\text{Weight of grafted product} - \text{weight of original sample} \times 100}{\text{Weight of original sample}}$$

Kraft Pulp

The 500-gram samples (oven-dry weight) of a sweetgum kraft pulp before and after bleaching were reacted separately at 3 percent consistency with a 6 percent

³The stock solution of ceric ion is prepared just prior to use because of the instability of the nitrate form.

Table 1.--Physical properties of bleached and unbleached paperboards treated
with varying concentrations of aqueous acrylonitrile

Sample	Thickness	Weight	Acrylonitrile concentration	Ring crush in cross-machine direction		Dimensional movement cross-machine direction	
				50 percent relative humidity	90 percent relative humidity	30 to 90 percent relative humidity	30 percent relative humidity to wet
	<u>Mils</u>	<u>G. per sq. m.</u>	<u>Pct.</u>	<u>Lb.</u>	<u>Lb.</u>	<u>In.</u>	<u>In.</u>
Unbleached linerboard:	10.8	190	0	63	28	1.20	2.79
Do.....	11.3	193	2	73	34
Do.....	11.1	186	4	91	40
Do.....	11.7	189	6	99	64	1.22	2.75
Do.....	11.3	217	(1)	132	60
Bleached cardstock :	6.6	151	0	38	18	1.35	3.47
Do.....	8.6	226	2	1.27	2.98
Do.....	9.8	181	488	1.57
Do.....	10.9	202	6	64	40	.85	1.37

¹Treated at the size press of paper machine with solution of starch and phenolic resin, the amount taken up being 14.4 percent based on original weight of board.

aqueous solution of acrylonitrile using ceric ammonium nitrate as the catalyst. The pulp slurry was thoroughly dispersed in a 10-gallon stoneware crock using a laboratory mixer equipped with a 4-inch impeller. The system was deaerated for 15 minutes with carbon dioxide and then the acrylonitrile was added. After deaeration for an additional 15 minutes, the necessary amount of 0.1 molar ceric ammonium nitrate and 1.0 molar nitric acid was added to give a final concentration of 0.005 molar and 0.05 molar, respectively. When the bleached pulp was thus treated, the viscosity and temperature of the pulp suspension increased immediately. Duration of immersion for each experiment was 20 minutes. The treated samples were washed thoroughly with warm water and then dried to a constant weight at 105° C. in a forced-draft oven. The weight increases were expressed as percent polymer pickup.

Results and Discussion

Treated Paperboards

The bleached cardstock, treated with a 6 percent solution of acrylonitrile, had a 30 percent polymer pickup. The amount of pickup for the unbleached linerboard, treated under the same conditions, was negligible. The low reactivity of the linerboard is attributed to a selective and rapid reaction between the lignin in the fiber and the catalyst, the lignin presumably being oxidized.

Compared to the untreated paperboards there was little or no difference in board appearance at the 2 and 4 percent levels of acrylonitrile concentration. However, at the 6 percent level, the cardstock was slightly yellowish in color, with a drop in brightness from an original 85.5 percent to 78.2 percent. This same board was noticeably harder and stiffer also. The appearance of the linerboard remained the same at all levels of treatment. The linerboard treated with a 6 percent solution of acrylonitrile was also harder and stiffer than the untreated board but, in addition, was extremely brittle. Because of this brittleness it would be impractical to treat unbleached paperboards with acrylonitrile when better strength and boardmaking qualities can be obtained by treating with a starch-phenolic resin mixture (table 1).

Ring crush data show that there were definite increases in the resistance to compression of the treated paperboards (table 1). When exposed at 90 percent relative humidity, the compressive strength in the cross-machine direction of the 6 percent-treated cardstock was 122 percent higher than that of the untreated boards. The compressive strength of the linerboard similarly treated was 129 percent higher.

Table 2.--Strength values of sweetgum kraft pulps before and after treatment with a 6 percent aqueous solution of acrylonitrile

Sample of sweetgum kraft pulp	Time beaten	Freeness (Canadian Standard)	Density	Burst factor	Breaking length	Folding endurance	Tear factor
	<u>Min.</u>	<u>Ml.</u>	<u>G. per cc.</u>		<u>M.</u>	<u>Double folds:</u>	
Unbleached, untreated	0	680	0.57	31.1	6,120	22	136.7
	15	520	.64	54.7	9,230	298	107.6
	20	400	.70	65.8	9,840	414	97.3
	20	400	.70	65.0	9,900	410	97.0
	30	210	.76	64.8	9,150	863	88.6
Unbleached, acrylonitrile treated	0	690	.54	25.5	5,580	14	114.3
	15	550	.60	43.3	7,530	100	113.5
	22	400	.66	57.0	8,000	360	88.0
	25	365	.68	58.3	8,020	446	92.8
	30	260	.70	56.6	8,560	584	90.6
Bleached, untreated	0	690	.54	24.1	5,240	14	112.4
	15	520	.65	54.3	8,730	238	109.6
	20	400	.68	60.0	9,700	400	102.0
	25	320	.70	61.2	9,840	466	97.4
	30	230	.75	60.5	9,530	929	91.7
Bleached, acrylonitrile treated:	0	780
	20	655	.33	1.8	582	.0	15.1
	25	400	.39	2.5	600	.0	15.0
	30	390	.39	2.4	666	.0	15.1
	35	255	.42	2.8	765	.0	16.0

Dimensional stability of the cardstock improved considerably (table 1) after treatment with 6 percent acrylonitrile. By subjecting the board to a change in relative humidity from 30 to 90 percent and thus increasing its moisture content, the stability of the board increased by 37 percent. When exposed at 30 percent relative humidity to completely water soaked, the stability of the board increased by 66 percent. There was no improvement in dimensional stability of the linerboard at any of the levels of concentration used.

Sweetgum Kraft Pulp

The results of experiments on the paperboards indicated that the total effect of treatment on the qualities of the kraft pulp, before and after bleaching, could be achieved using a 6 percent concentration of acrylonitrile.

Unbleached kraft pulp.--The unbleached kraft pulp had only a 12 percent pickup of polymer and was slightly lighter in color than the original pulp. This low reactivity was again attributed to the lignin present in the unbleached fiber. Strength of this pulp except for breaking length, which was 19 percent lower, averaged only 13 percent less than the untreated pulp at a freeness of 400 milliliters Canadian Standard (table 2).

Bleached kraft pulp.--The bleached kraft pulp had 135 percent polymer pickup. The reaction product was highly hydrophobic, as was manifested by the rapid drainage of water from it. The product resembled short asbestos fibers and gave a rasping sound when squeezed between the fingers.

Test results of the strength properties of the bleached kraft pulp show a considerable loss in strength due to the treatment. At a freeness of 400 milliliters Canadian Standard, burst was reduced 96 percent, breaking length 92 percent, fold 100 percent, and tear 95 percent from that of the untreated pulp. These results show that the bonding capacity of the treated fibers was completely destroyed.

It is well-known that in a fibrous medium such as pulp, scattering of light occurs mainly at the cellulose-air interfaces. These include outer surfaces of the fiber, lumen surfaces, fibrils and other particles, and at voids in the cell wall of the fiber. The data in table 3 show that as the percent of treated fibers in a sheet is increased, the scattering coefficient of the pulp is decreased, as is brightness. This sharp decrease in the scattering coefficient is due to the filling up of these cellulose-air interfaces with homopolymer, which decreases the fiber-to-fiber bonding capacity in spite of the fact that the synthetic polymer has the ability to form hydrogen bonds.

Table 3.--Effect of acrylonitrile treatment on scattering coefficient of bleached kraft pulp

Percent treated pulp mixed with untreated pulp :	Brightness :	Reflectance (R_o) :	Reflectivity (R_{oo}) :	Opacity ($C_{0.89}$) :	Scattering coefficient (s) :
	<u>Pct.</u>				
20	81.1	67.5	89.5	74.4	360
40	80.1	64.9	89.5	72.8	325
60	80.3	67.2	90.0	76.0	309
80	78.1	59.3	88.0	65.5	281
100	78.2	59.4	68.1	237

Refractive indices of the bleached pulp were determined using the Becke Line Technique which was accurate to ± 0.001 in this study. The refractive index (η) of the treated fiber was lower in both directions as shown in the following tabulation.

<u>Pulp sample</u>	<u>Refractive indices</u>		<u>Birefringence</u> (max. η - min. η)
	<u>Maximum</u>	<u>Minimum</u>	
Untreated	1.575	1.535	+0.040
Treated	1.534	1.517	+0.017

These data provide for a better understanding as to why acrylonitrile-treated fiber has improved dyeability. Dyes will normally penetrate or diffuse more rapidly through a cellulose fiber of low orientation than through cellulose fiber of high orientation. Birefringence is a measure of orientation, and the larger the birefringence the greater the molecular orientation in the fiber. In this study the untreated fiber shows greater molecular orientation than the treated fiber. The decrease in birefringence or orientation is caused by the buildup of homopolymer around the fiber.

Resistance of the fibers to chemical attack was enhanced by treatment with acrylonitrile. Untreated fiber went into solution almost immediately in 1.0 molar cupriethylenediamine, whereas the treated fiber was insoluble. Microscopic examination of the treated fiber in the cupriethylenediamine showed very little swelling and seemingly only where the fiber was bent or appeared to have been damaged. Apparently the chemical bond between polymer chains, within the homopolymer around the fiber, is strong enough to restrain any swelling of the fiber cell wall.

Another property affected by the treatment was the hygroscopic relation between cellulose and moisture. Pulp pads, 5.0 grams oven-dry weight, of the bleached pulp before and after treatment were placed in an atmosphere conditioned to 75° F. and 50 percent relative humidity and allowed to come to equilibrium. Results showed that the untreated pulp pads reabsorbed an average of 65 percent more moisture during the time required for the pads to attain equilibrium. Thus the cellulose fiber becomes much more hydrophobic after treatment with acrylonitrile.

Extraction of Treated Bleached Kraft Pulp

To determine the degree of actual grafting of acrylonitrile to the cellulose fibers it is necessary to separate the homopolymer from the copolymer. Dimethylsulfoxide and dimethylformamide, reputed to be adequate solvents for acrylonitrile, were used in this study. After treatment with acrylonitrile, a sample of the bleached kraft pulp was extracted with dimethylsulfoxide at 35° C. for 24 hours and another sample was extracted at 95° C. for 24 hours. These extractions removed only 5.5 and 9.7 percent of the polymer respectively. Extraction with dimethylformamide at room temperature for 24 hours removed only 3 percent of the polymer. Both solvents converted the pulp to a gel-like mass that was slimy to the touch.

Pure samples of acrylonitrile homopolymer were then extracted with dimethylsulfoxide and dimethylformamide to determine the effectiveness of these solvents. For reactions at room temperature and higher, the homopolymer merely swelled to a gel-like substance (similar to the pulp extractions) rather than dissolving in the solvents. Figures 1 and 2 show the gel obtained by extracting the homopolymer with dimethylsulfoxide at 95° C. for 24 hours. This gelatinous mass remains stable at these high temperatures.

These results showed that both dimethylsulfoxide and dimethylformamide were ineffective in dissolving the homopolymer from the treated pulp. However, the gelatinous material which characterized the extractions of both the treated pulp and the pure homopolymer suggested that largely homopolymer was formed around the fibers with very little actual grafting.

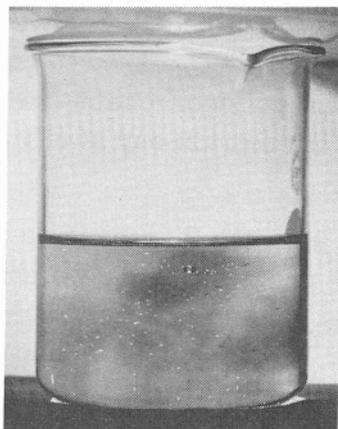


Figure 1.--Acrylonitrile homopolymer after heating in dimethylsulfoxide at 95° C. for 24 hours. Air bubbles are at the interface of the swollen polymer and dimethylsulfoxide solution.

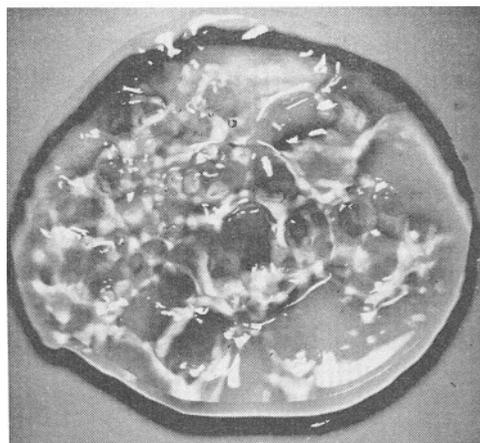


Figure 2.--Swollen mass of homopolymer from figure 1 after dimethylsulfoxide was decanted off.

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To strengthen the belief that little if any grafting occurred, D-glucose was used as a model compound for reaction with acrylonitrile. Since D-glucose will undergo the same chemical reactions as cellulose and is soluble in water, no physical entanglement of homopolymer could occur because glucose has no fibrous material.

During the glucose-acrylonitrile reaction a very small amount of solid was formed, but it was not measured quantitatively. Analysis of the filtrate for total reducing sugar showed 99.0 percent unreacted glucose, or 1.0 percent unaccounted for. Chromatographic analysis showed 99.3 percent unreacted. However, this apparent evidence of about 1 percent of glucose grafted to the carbohydrates cannot be fully accepted because this amount is within the experimental variation of the analytical method.

The findings of this study support the credence that little actual grafting of acrylonitrile to the cellulose molecule occurs. Instead, the voids in the cell wall are filled with the homopolymer first and as the reaction continues, there is a constant buildup of homopolymer around the cell wall. This conclusion is contrary to that of Daniel and coworkers (1) who, on the basis of a similar study, reasoned that any unextractable polymer was chemically combined with the cellulose to form a graft copolymer.

Conclusions

It has been shown that physical, chemical, and optical properties of the bleached paperboard and pulp fiber have undergone considerable change due to treatment with acrylonitrile. The presence of lignin in the fiber decreased the amount of polymer takeup.

Treatment of cellulose fiber in sheet form is the better method with respect to strength properties because the bonding capacity of the bleached pulp treated in suspension was completely destroyed.

Despite the marked changes in product qualities of the bleached, treated material, it is believed that little, if any, grafting of acrylonitrile onto the cellulose molecule occurs with the system used in this study. Rather, the monomer polymerizes with itself and is located physically on the fiber surfaces and within the cell wall voids as a homopolymer.

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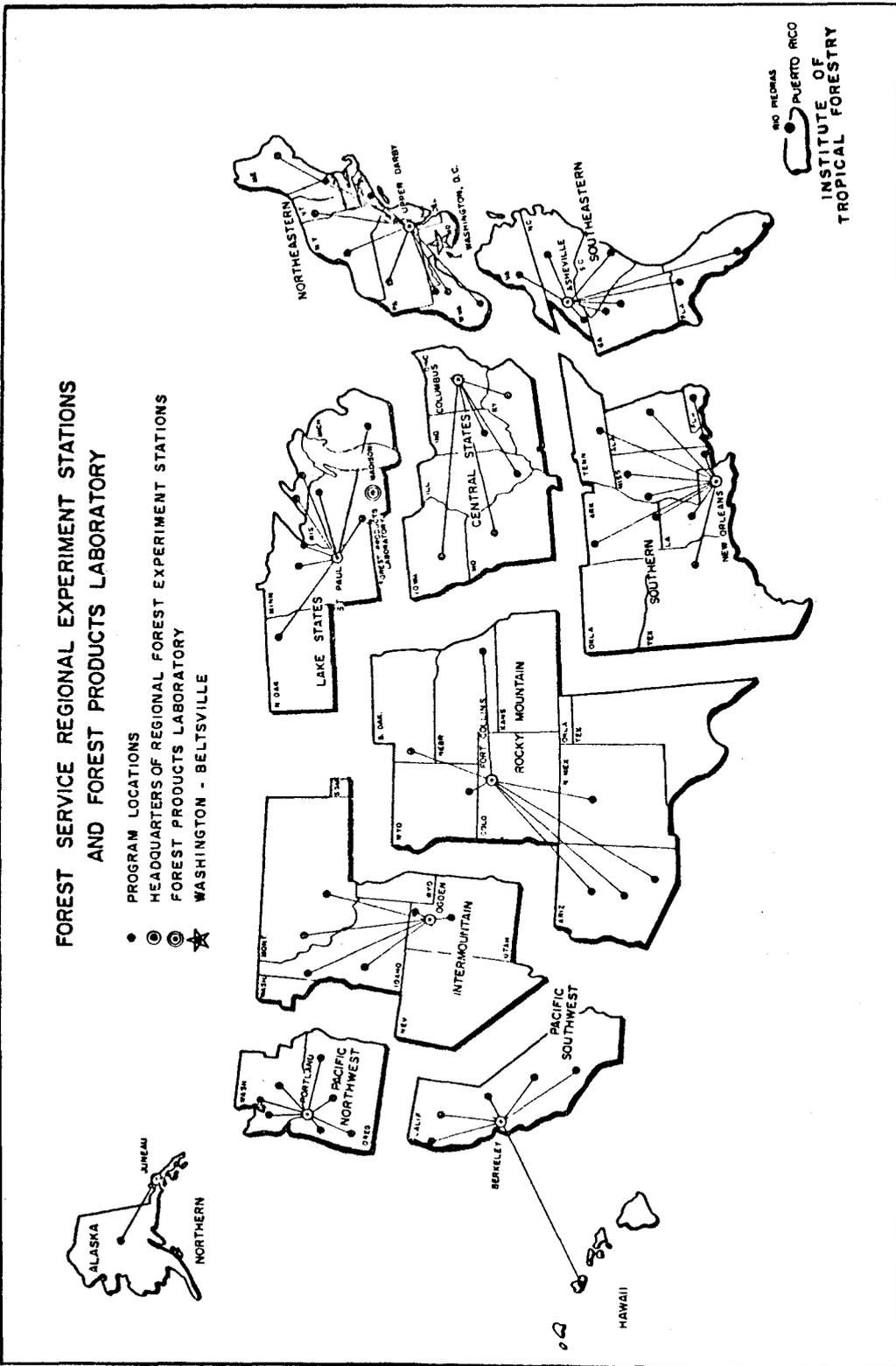
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