

GRAFT POLYMERIZATION. III. SOME PROPERTIES OF THE LEATHER OBTAINED FROM THE GRAFT POLYMERIZATION OF VINYL MONOMERS ONTO CHROME-TANNED NIGERIAN HAIRSHEEP*

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ABSTRACT

This study reports the physical and chemical properties of chrome-tanned sheepskins after graft polymerization with 12 vinyl monomers, alone or in combinations. These graft copolymers (collagen plus synthetic polymer) can be made to contain as much as 50 percent by weight of synthetic polymer and still have the natural appearance of leather. This work indicates that these increased quantities of grafted synthetic polymer modify leather to a proportionally greater degree. The type of modification depends on the nature of the grafted synthetic polymer. Increases in thickness, up to 93 percent, are obtained without apparent loss in area. Stretch was increased except when methacrylates or styrene were grafted. Break load increased in all but two examples. Since the thickness usually increased to a greater degree than the break load, the tensile strength was not always increased, although the leather was actually stronger.

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INTRODUCTION

Our initial studies demonstrated the feasibility of graft polymerizing vinyl monomers onto chrome-tanned sheepskins (1). From the results obtained with the few monomers investigated in those studies it was found that the grafted polymer, even when present in a relatively small amount, could lend its particular properties to the substrate. We thereby demonstrated the potential of this process for modifying the properties of the resulting leathers in a controlled manner for achieving certain properties that were not previously possible in leather. Since these initial studies, the graft polymerization procedure has been improved to the

point that graft copolymers can now be made which contain up to 50 percent synthetic polymer by weight but still retain the natural appearance of leather (2). Therefore, the properties of the synthetic polymer can be imposed to an even greater extent on the final leather.

The properties that may be attainable could vary widely because of the large number of vinyl monomers available commercially. These may be used singly or in combination. This paper gives a preliminary report of some selected physical and chemical properties of the graft copolymers made by the graft polymerization of 12 monomers onto chrome-tanned sheepskins.

The physical properties chosen for investigation were tensile strength, as a measure of the graft copolymer's integrity, and the Williamson torsion test, as a measure of the graft copolymer's stiffness.

The monomers used were chosen for their ready commercial availability and for the range of properties exhibited by their respective polymers. For example, butyl acrylate forms a polymer which is of a soft, rubbery nature, while methyl methacrylate or styrene form relatively hard, strong polymers.

EXPERIMENTAL

Materials and Procedures

Commercially chrome-tanned Nigerian sheepskins were washed, drained, and cut into one inch to 1-1/4 inch wide strips across the entire width of the skin. These strips were numbered consecutively from rear to front of skin. The odd-numbered pieces were used as controls and the even-numbered pieces were used for the graft polymerizations.

The low inhibitor grade monomers were obtained from the usual commercial sources and were used as obtained. These are listed in Table I. No attempt was made at further purification. The other materials used in the graft polymerizations, as well as the procedure itself, were discussed in our previous publication (2).

Preparation for Physical Testing

The control and graft copolymer strips were dehydrated in absolute methyl alcohol, which was changed twice each day over a period of several days until the specific gravity of used solvent equaled that of fresh solvent. The strips were then laid flat in a fume hood between layers of towels to prevent condensation of moisture on them while air drying. When dry, all the strips were conditioned at 50 percent relative humidity and 23°C. before physical testing.

Physical Tests

The tensile strength determinations were made according to the accepted procedure (3) on test pieces cut from the one inch to 1-1/4 inch strips of sheepskin

TABLE I
MONOMERS INVESTIGATED

Monomer	Inhibitor, p.p.m.	Source†
Acrylonitrile	MEHQ	30-45 A
Styrene	TBP	15 B
Divinylbenzene	TBP	4 C
Ethyl acrylate	MEHQ	15 D
Butyl acrylate	MEHQ	5 D
Methyl methacrylate	MEHQ	10 D
2-Ethylhexyl acrylate	MEHQ	50 B
Butyl methacrylate	MEHQ	10 D
Acrylic acid	MEHQ	200 D
Methacrylic acid	MEHQ	100 D
Ethylene diacrylate	MEHQ	50-100 B
Ethylene dimethacrylate	HQ	50-140 B

*MEHQ = Monomethyl ether of hydroquinone
 TBP = *t*-Butyl pyrocatechol
 HQ = Hydroquinone

†A = Matheson, Coleman and Bell‡
 B = Monomer-Polymer Laboratories
 C = J. T. Baker Chemical Company
 D = Rohm and Haas

‡Reference to brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

stock on one side of the backbone, and most were made, in duplicate, perpendicular to it. For measuring stiffness, the standard Williamson torsion test (4) was used on pieces of the same strips but from the opposite side of the backbone. This test was modified to accommodate our heavier weight stock by replacing the recommended 0.010" diameter wire with one of 0.014" diameter.

Analyses

The amounts of total, extractable, and bound (unextractable) polymer were determined by the techniques described in our earlier publication (2).

Polymer Extractability with Stoddard Solvent (Simulated Drycleaning)

Approximately one g. (accurately weighed) of analyzed, air-dried graft copolymer was shaken for 30 minutes at room temperature in 100 ml. of Stoddard solvent. This mixture was then filtered and the extracted graft copolymer was washed on the funnel with 25 ml. of fresh Stoddard solvent. The filtrate and washings were transferred to a tared crystallizing dish and the filter flask was rinsed with an additional 25 ml. of fresh Stoddard solvent which was added to the material in the crystallizing dish. The contents of the crystallizing dish were

evaporated to dryness on the steam bath under a stream of air and the residue was then dried at 110°C. for 16 hrs. This entire procedure was performed three times on each graft copolymer. The Stoddard solvent used in these extractions itself left a residue of 11 mg./150 ml. upon evaporation under the same conditions as above; therefore, the results obtained for each extraction were corrected for this value.

RESULTS AND DISCUSSION

The two physical tests chosen for application to the graft copolymers made in this study yielded more than just the tensile strength and stiffness data. The tensile strength test gave, in addition to the strength, a measure of the stretchiness of the material. For both tests, thickness measurements were required. Thus, the combined information from these two tests can be used to select the graft polymerization products for further investigation.

The solvent dehydration technique was chosen as the means of preparing both the graft copolymers and the control strips for physical testing, since we sought to compare the properties of the treated leathers against those of the controls in the most direct manner possible, uninfluenced by the effects of fatliquoring. In all likelihood, a fatliquor suitable for the controls would not necessarily be the best for each of the 26 graft copolymers studied. Methyl alcohol was chosen as the dehydrating solvent because it was a very poor solvent for the polymers but an effective dehydrating agent.

The graft copolymers made, their analyses, and the results of the physical tests are all given in Table II. The first column lists the monomers. The theoretical yield of synthetic polymer resulting from the low (L) level of application corresponds to a product with approximately 29 percent total polymer. The theoretical yield of synthetic polymer resulting from the high (H) level of application corresponds to a product with approximately 50 percent total polymer. The experimentally obtained yields are given in Column 2 of Table II. The percentages in the second and third columns refer to the percent by weight of the graft copolymer. Thus, a value of 50 percent in Column 2 refers to a graft copolymer which is 50 percent chrome-tanned sheepskin and 50 percent synthetic polymer, while a value of 25 percent in Column 3 for the same product would indicate that one half of this synthetic polymer was extractable and the other half was not.

The amount of total polymer in the graft copolymer products at the low level of application of monomer or monomer mixture varied from 17 percent for poly(ethyl acrylate) to 33 percent for poly(methyl methacrylate) and also with cross-linked polystyrene. These correspond to yields of polymer of 59 percent and 114 percent, respectively. (Values over 100 percent can be explained by the variation in the amount of hide substance in any given piece of wet stock.) The amount of total polymer in the graft copolymer products at the high level of application of these same monomers or monomer mixtures varied from 32 percent for poly-

Monomer(s)*	Percent Polymer†				Percent Change, in‡									
	Total		Bound		Thickness		Stretch		Break Load		Tensile Strength		Relative Stiffness††	
	L**	H**	L	H	L	H	L	H	L	H	L	H	L	H
Acrylonitrile	22	32	21	31	11	78	14	0	20	47	-22	-6	+	++
Styrene	24	45	11	12	22	81	-21	-8	22	19	4	-36	+	+
Styrene + Divinyl- benzene	33	53	32	52	74	119	-20	-14	44	16	-18	-44	++	+
Ethyl Acrylate	17	41	13	28	6	39	27	44	23	77	14	27	0	+
Butyl Acrylate	31	44	13	16	14	43	33	160	17	70	8	9	0	--
Methyl Methacrylate	33	50	13	16	32	70	6	-8	23	24	0	-30	+	++
Butyl Acrylate + Acrylic Acid	29	49	27	49	34	70	58	88	41	27	5	-30	0	0
Butyl Acrylate + Ethylene Diacrylate	24	47	23	45	42	93	52	80	31	59	-44	-19	0	0
Butyl Acrylate + Methyl Methacrylate + Acrylic Acid	31	37	28	33	22	39	0	-22	6	-12	-14	-37	+	+
Methyl Methacrylate + Methacrylic Acid	27	54	26	49	9	88	0	-16	7	7	-6	-37	+	++
Methyl Methacrylate + Ethylene Dimethacrylate	30	49	29	45	33	47	0	-21	10	28	-16	-14	+	+
2-Ethylhexyl Acrylate		1		0		2		-7		17		13		0
2-Ethylhexyl Acrylate + Acrylic Acid		36		26		19		28		29		10		0
Butyl Methacrylate		4		2		8		-22		6		0		0
Butyl Methacrylate + Methacrylic Acid		43		40		87		-24		-33		-64		+

*In binary compositions a ratio of 23 parts of the first monomer to two parts of the second monomer was used. This mixture was applied at the low and high levels. The ternary composition was made in the ratio of 12:12:1 and applied at each level.

†Percent polymer is a weight percent calculated on a moisture-free and ash-free basis. Total polymer is calculated from the nitrogen analyses of control and treated pieces. Bound polymer is obtained by correcting the total polymer for the amount extracted by ethyl acetate.

‡Percent change was calculated by averaging the data from adjacent control strips and dividing this into the data for the treated strip and multiplying by 100.

**In all columns L is the low level of application and H is the high level. For the low level, the total monomer offered was 40 percent of the dry weight of chrome-tanned skin. For the high level the total monomer offered was 100 percent of the dry weight.

††Control and test data from the Williamson stiffness test were handled as in the third footnote (‡). If the change was ± 15 percent the symbol 0 was used to indicate no change. An increase up to 100 percent was considered stiffer (+). Values over this were considered much stiffer (++). The one decrease in stiffness was great enough to require the symbol (--).

acrylonitrile to 54 percent for the methyl methacrylate-methacrylic acid copolymer. These values correspond to about the same range in yields of polymer as was found for the low level of application of monomer. 2-Ethylhexyl acrylate and butyl methacrylate, which were applied at the high level only, gave essentially no polymer when used alone. However, when used with the corresponding acid (acrylic and methacrylic, respectively), the yields of polymer were comparable to those obtained with the other monomers. Thus, under the conditions used, all the common monomers, with the exceptions noted above, polymerized readily in the chrome-tanned sheepskins. In most cases there was very little or no formation of homopolymer in the floats or on the surfaces of the skins.

The amount of bound (unextractable) polymer in the graft copolymer products (with the exceptions of the products made with those monomers that did not polymerize) varied from 11 percent (for the low level polystyrene) to 52 percent (for the high levels of the styrene-divinylbenzene copolymer). It is obvious that in these products the amount of total polymer depended on the level of application of monomer or monomer mixture, while the amount of bound polymer depended on the nature of the monomer or monomer mixtures, as well as on the level of application. Calculated as a percent of the total synthetic polymer present in the products, the amount of bound polymer varied from 27 percent (for the high level polystyrene) to 100 percent (for the high level of the butyl acrylate-acrylic acid copolymer). Possible reasons for this will be discussed later.

The thickness results reported in Column 4 of Table II are expressed as percent change in thickness and, in all cases, were positive, indicating an increase in thickness as compared with the control. These values were obtained by comparing the averages of the data from the thickness measurements on the given graft copolymer specimens in both the tensile strength test and the Williamson torsion test with the averages of the corresponding data from both neighboring control strips. These increases in thickness were, in general, greater for the products made with a high level of monomer and were not accompanied by a loss of area. They are apparently more related to total polymer than they are to bound polymer. There was no visible deposition of synthetic polymer on the surfaces nor in the open structures of the products.

The extent to which a test strip stretched before breaking is reported in Column 5 of Table II as the percent change relative to the control strips on either side. Owing to the variability of the stock, a change of ± 10 percent is probably not significant. The values obtained, however, correlated quite well with what was expected for the corresponding synthetic polymers themselves. The use of acrylonitrile, styrene, or methyl methacrylate produced leathers with low values for extension at break. The use of butyl acrylate or ethyl acrylate alone consistently gave products which showed significant increases in this property. The high level of butyl acrylate better than doubled it.

The percent change in load at which the graft copolymer products broke and

the resulting percent change in tensile strength are reported in Columns 6 and 7, respectively, of Table II. In keeping with our desire to compare, as directly as possible, the effects of the graft polymerization, we are presenting both these values. The graft polymerizations caused increases in both the thickness (up to 119 percent) and the break load (up to 77 percent). There were only two decreases in this latter property (leathers made with high level of butyl acrylate-methyl methacrylate-acrylic acid terpolymer and the high level of butyl methacrylate-methacrylic acid copolymer). Even so, unless the break load increased (on a percentage basis) as much or more than the thickness, a decrease in tensile strength resulted, as was observed in most cases. In 20 out of the 26 examples the percent change in break load increased by ten percent or more, yet only eight out of the 26 examples had increased tensile strengths. Some of the samples that showed reduced tensile strengths actually had increases of about 50 percent in the break load.

Data on stiffness (as determined by the Williamson test) are given in Column 8 of Table II in the form of the symbols +, -, and 0. This system was chosen because of the variability of the results. Also, since these samples were not fatigued, the actual numbers have no direct relation to commercial leathers. Only one of the grafted copolymers showed a decrease in stiffness. It was made with the high level of butyl acrylate and was quite flexible (- -). Again, the results obtained for these graft copolymer products were those expected from the different monomers used.

Next, we shall discuss the individual products themselves and evaluate their potential for continued study and possible application to the manufacture of specific types of leather. It is a little premature to go too far into the latter but some preliminary indications are available.

Polyacrylonitrile itself is hard and brittle, has a high softening point, and is very resistant to chemical attack. It is also quite insoluble in most common solvents. In the presence of plasticizers it is tough and considerably less brittle. The two graft copolymer products containing this synthetic polymer had properties more or less consistent with those of polyacrylonitrile. Our inability to extract any homopolymer was probably due more to its insolubility in ethyl acetate (or any other common organic solvent) than to its greater degree of attachment to the protein. Although the overall results obtained with this monomer were comparable to those obtained with other monomers or monomer mixtures, its low boiling point and its high toxicity did not indicate any need for further investigation.

Polystyrene has properties somewhat similar to polyacrylonitrile except that it is thermoplastic and quite soluble in many common organic solvents. Less than half of the polystyrene in the two products containing it was bound and the other properties, especially those of the product made with the high level of styrene, gave little cause to recommend further investigation. Replacing a small part (eight percent) of the styrene with divinylbenzene (a cross-linking agent) gave little improvement except that the extractability was essentially eliminated. This latter

was probably due more to the insolubility of the synthetic polymer (now cross-linked) than to an increase in the extent of grafting.

The use of the ethyl acrylate was included mainly for comparison purposes since its toxic and lachrymatory nature would prohibit its use in a tannery. The two graft copolymers which were obtained, however, were very promising and it is unfortunate that this monomer is afflicted with these adverse properties.

The butyl acrylate alone gave in many respects the best products. These had moderate increases in thickness, substantial increases in stretchiness, and good increases in strength. These results confirm those reported previously (1, 2). The high level of application gave a product which was extremely mellow and stretchy, properties which we feel would be beneficial in garment leathers.

Methyl methacrylate gave a product which was very much like that obtained with acrylonitrile; however, this monomer is considerably less toxic. From the preliminary results obtained in this study concerning the firmness, nonstretchability, and strength of the products, we feel that this monomer should have some application in the production of shoe upper leathers.

Butyl methacrylate and 2-ethylhexyl acrylate graft polymerized very poorly under our conditions and the products obtained warrant little mention.

In the hope of enhancing the proportion of the synthetic polymer which was unextractable we investigated the use of small amounts of two acidic monomers, acrylic acid and methacrylic acid, and two cross-linking monomers, ethylene diacrylate and ethylene dimethacrylate, in these formulations. We have already alluded to the effectiveness of this in the discussion of data in Column 3 in Table II and of the product made with styrene-divinylbenzene. These additional monomers were used in place of only a small fraction (eight percent) of the usual monomer but their effects were dramatic and not always beneficial as far as some physical properties were concerned. Very little homopolymer could be extracted from any of these products. The importance of this will be discussed later; at this point we would like to discuss the possible reasons for it. Perhaps the most obvious explanation would be that we have decreased the solubility of the homopolymers in the solvent used for the extraction. This was the explanation we gave for our inability to extract any homopolymer from the polyacrylonitrile graft copolymer and from the copolystyrene-divinylbenzene graft terpolymer. In the present case, however, we have investigated the solubility of the corresponding synthetic polymers in ethyl acetate and those synthetic polymers containing the acidic monomers were sufficiently soluble that insolubility is not the explanation. The cross-linked synthetic polymers were indeed insoluble but they were dispersible in the ethyl acetate to the extent that they passed through the Soxhlet extraction thimble. With these results in mind, we offer the following explanations for consideration.

First, for those graft copolymers made with the acidic monomers, we feel that

the synthetic polymer is held in the product by a combination of covalent and ionic bonds to the chrome-tanned hide protein. Second, for the cross-linked graft copolymers, we feel that we may have produced an interpenetrating polymer network (IPN) (5) with the cross-linked chrome tanned hide protein and cross-linked synthetic polymer interpenetrating each other's cross-linked segments. These explanations are under further investigation.

Both the acidic monomer and the cross-linking monomer had similar effects on the properties of the graft copolymers obtained with butyl acrylate. In comparison with the graft copolymers obtained with butyl acrylate alone, these products had greater increases in thickness at both levels of application. Increases in extension at break were greater at the lower levels of application and less (by 50 percent) at the higher levels of application. The same trend was found in the break load. The great reduction in stiffness observed with the high level of butyl acrylate alone was lost in these products. Therefore, the gain in the unextractability of the synthetic polymer was achieved at the sacrifice of some of the other physical properties. The changes in the various properties caused by the use of methacrylic acid or ethylene dimethacrylate with methyl methacrylate were of a nature similar to those just discussed for the various butyl acrylate combinations. The only dramatic improvement was in the unextractability of any synthetic polymer. The three-way combination of butyl acrylate-methyl methacrylate-acrylic acid gave, at the high level of application, one of the two products exhibiting a decrease in break load. The other properties, except unextractability, were also poor.

Finally, the use of the acidic monomers with the 2-ethylhexyl acrylate or butyl methacrylate caused these two previously recalcitrant monomers to graft polymerize readily under our conditions. Both gave products with very little extractable synthetic polymer. The product obtained with the 2 ethylhexyl acrylate-acrylic acid combination had reasonably good properties, while that obtained with the butyl methacrylate-methacrylic acid combination had some of the poorest properties of any product examined thus far.

Because of the properties we have found in the poly(butyl acrylate)-containing products, namely, the stretchiness, strength, and mellowness, we have felt that these products should find some use as garment leathers. We have, therefore, investigated the Stoddard solvent extractability of the synthetic polymers from the graft copolymers listed in Table III. These three products were made with the high level of monomer and all contained about 50 percent synthetic polymer. The amount of bound polymer was determined and found to be similar to that obtained with the three corresponding products made earlier and listed in Table II. The results given in Columns 4 through 7 for percent extractables were obtained with the Stoddard solvent under conditions simulating drycleaning (see Experimental). As is evident from these results, most of the unbound poly(butyl acrylate) was extracted by the Stoddard solvent while very little of the acidic or cross-linked polymers was. Thus, it may be possible to produce a drycleanable garment

TABLE III
POLYMER EXTRACTABILITY WITH STODDARD SOLVENT
(Dry Cleaning Simulation)

Monomers*	Percent† Polymer		Percent Extractable at Each Cycle			
	Total	Bound	1st	2nd	3rd	Total
Butyl Acrylate	48	20	11.2	6.0	2.5	19.7
Butyl Acrylate + Acrylic Acid	52	44	2.5	0.3	0.2	3.0
Butyl Acrylate + Ethylene Diacrylate	50	48	0.5	0.3	0.0	0.8

*All monomer(s) were applied at the high level, *i.e.*, equal to 100 percent of the dry weight of chrome-tanned skin. The binary compositions were in the ratio of 23:2 and this mixture applied at the high level.

†Percent polymer is a weight percent calculated on a moisture and ash-free basis. The total polymer is calculated from the nitrogen analyses of the control and treated pieces. Bound polymer is obtained by correcting the total polymer for the amount extracted by ethyl acetate.

leather if the undesirable effects of the acidic or cross-linking monomers are balanced by the desirable effects.

CONCLUSIONS

As a result of evaluating the many leathers produced by interacting various monomers with chrome-tanned hide, the most promising products were obtained from the use of butyl acrylate and methyl methacrylate. This is especially so for the combination treatments based on these two monomers and incorporating an acidic or cross-linking co-monomer. It is most probable that the final recommendation will be a combination treatment that involves a compromise of the properties of several different monomers. Some further indications that this will be so are already in hand and will form the basis of further publications.

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DISCUSSION

DR. WILLIAM PRENTISS (Rohm and Haas Company): I feel it is a pleasure and an honor to serve as Discussion Leader for a paper of this nature because it represents a continuing series of explorations into new ways of working with a basic and old raw stock, leather, to produce in it some new and interesting properties. Ed, thanks very much for your presentation. Interesting to me was that the properties that were recorded as a function of the types of monomers used fall pretty much in line with what might be expected from normal polymers made from these particular monomers. They are not exactly in line, but nonetheless they do follow the same general pattern. There were some interesting observations, however, such as the thickness increase. As you proceeded from the "low" and "high" level of monomer, the thickness showed a tremendous change. Do you have any speculation as to why you would see such a large change in the thickness as you go from approximately 30 to 50 percent monomer?

E. H. HARRIS (Eastern Regional Research Laboratory, USDA): As you said, speculation, and that is all that it would be. Apparently the polymerization takes place around the actual collagen chain. This prevents the sample from collapsing and glueing together on drying. Why one sample with the high level of butyl acrylate compared to the low level should give such a large change, I cannot honestly say. We've noticed this change. I would like to point out that, even though we made no direct measurements as to area, there were no visible losses in area. These were relatively narrow strips. When we went to cut out the tensile strength test strips there was at that point sufficient width for the sample. I think that is about where I would have to let this matter rest.

DR. PRENTISS: I think that the latter part of your comment is an important one, when you stated that your area loss was minimized or essentially nil, even though you got tremendous increases in thickness. This is not a usual observation when one goes through increases in plumping or thickening in normal tanning procedures. Are there any other questions from the floor? (PAUSE) I have another comment or question I would like to pose to you, again more of a speculative nature. In an earlier paper from the USDA laboratory ("Graft Polymerization. II. Factors Affecting the Graft Polymerization of Vinyl Monomers Onto Chrome-Tanned Hide Substance" by A. H. Korn, *et al.*) it was indicated that the amino acid analysis shows that the grafting to amino acids does not explain the full extent of the combination of the polymer with the collagen or the chrome-collagen complex. In this work you report the influence of either ethylene diacrylate or one of the acrylic acids which increases the amount of bound or unrecovered polymer. I think it is fairly reasonable to understand why ethylene diacrylate might reduce extractability because of the crosslinking that it imparts to the polymer. Would you care to speculate what happens when you put acrylic acid into the system?

MR. HARRIS: Using acrylic acid, or, in some of the other runs, methacrylic acid, we introduced the carboxyl groups as functional parts of the polymer. As pure speculation, this could increase the binding of the polymer system to the collagen, either through ionic bonds with the collagen itself, or possibly with the chrome moiety present. This would act to insolubilize and tie up the polymer. We would have to do some experimental work to prove this.

DR. PRENTISS: Thank you very much, Ed. Are there any questions? I have one coming from the back.

MRS. JEAN J. TANCOUS (Tanners' Council Research Laboratory, Univ. of Cincinnati): Diluting the leather fibers with a retannage or filling materials usually decreases tensile strength. Why do you think there was an increase in tensile strength?

MR. HARRIS: If you remember, I did not say that it increased the tensile strength, because in calculating tensile strength you must take into account the thickness of the sample.

MRS. TANCOUS: It increased the load?

MR. HARRIS: It increased the break load. In some cases, due to the mathematics, there was an actual increase in the pounds per square inch as you would normally report tensile strength. These results may vary quite a bit, since the sample increased in thickness from a few percent in some cases to as high as 93 percent in the leathers showing the greatest thickness increases.

MRS. TANCOUS: It increased the break load, but most of the time it did decrease the tensile strength. That is what I wanted to know.

MR. HARRIS: Yes, in most of the cases the actual tensile strength was decreased because of this gain in thickness.

MR. RICHARD N. JONES (A. C. Lawrence Leather Co., Peabody, Mass.): You may have mentioned this in your presentation, in which case I missed it. I believe you said your specimens were cut widthwise across the skin, from belly to backbone. Is that correct?

MR. HARRIS: That is correct; so the tensile strength strips were perpendicular to the backbone.

MR. JONES: But at what portion of this long narrow strip were the tensile strength and other measurements made? Was it near the backbone or was it near the belly? In other words, I am interested in the uniformity or lack of it that you saw in the backbone portion *versus* the belly portion.

MR. HARRIS: The actual size of the skins used permitted us to get only two tensile strength strips out. As a result, one was essentially an inch or so removed

from the backbone and the other one was taken immediately below that, so it was closer to the belly area. There is some variability. Without having the actual test data at hand, I would say that there is probably less variability in the two locations on the treated samples compared to the control strips on either side.

MR. JONES: That is the point in which I was interested. Thank you.

DR. PRENTISS: Are there any further questions? I have one final one, Ed. Do you happen to have samples of some of the treated materials so that the people here could look at them later in the day?

MR. HARRIS: We have one relatively small sample, about five or six inches by eight inches, on which we used butyl acrylate as the grafting monomer. We also have a similar piece of the same chrome stock, as a control. Both of these, however, were lightly fatliquored, which differs from the reports that I have been giving here. The test samples that I used were not fatliquored.

DR. PRENTISS: Thank you again, Ed, for a very fine presentation and discussion. I think we owe the Eastern Regional Laboratory people a real vote of thanks for doing this fine work.