

GRAFT POLYMERIZATION. II. FACTORS AFFECTING THE GRAFT POLYMERIZATION OF VINYL MONOMERS ONTO CHROME-TANNED HIDE SUBSTANCE*

A. H. KORN, M. M. TAYLOR, AND S. H. FEAIRHELLER

*Eastern Regional Research Laboratory**
Philadelphia, Pennsylvania 19118*

ABSTRACT

It has been demonstrated that chrome-tanned animal hides and skins can be successfully treated with acrylic monomers in a graft polymerization process. This treatment is carried out in an aqueous emulsion under mild conditions using a redox system to generate free radicals as initiators of the graft polymerization. Such modified materials contained 15-20 percent of the graft polymer which is irreversibly bound and 20-30 percent homopolymer which is extractable with organic solvents. New properties were imparted which are not found in conventionally treated leathers, such as improved uniformity, increased thickness, and a greater internal lubrication.

The effect of a number of variables on the uptake of polymer has been examined in detail. These variables include monomer concentration, initiator concentration, amount of surfactant, sequence of addition of these components, and pH. In addition, the effects of various types of surfactants and reducing agents were studied, as was the pre-emulsification of the monomer. A study was also made to determine the differences in uptake of polymer in various parts of the hide.



INTRODUCTION

In the first paper of this series (1) it was shown that it was possible to graft polymerize ethyl and butyl acrylate onto chrome-tanned animal hides and skins. This blending of synthetic polymer with natural polymer resulted in the production of modified leathers with improved properties. It was shown that the chrome-tanned sheepskins and goatskins treated with butyl acrylate appeared to have a high degree of internal lubrication and a greater thickness and uniformity

*Presented at the 68th Annual Meeting of the American Leather Chemists Association, Pocono Manor, Pennsylvania, June 18-21, 1972.

**Agricultural Research Service, U. S. Department of Agriculture.

of grain than untreated skins. Such modification could eliminate some of the later costly finishing operations, such as retanning and impregnating, and may enable tanners to meet more successfully the challenge of synthetic substitutes for leather. In addition to these advantages it has been reported that sheepskin and goatskin can withstand considerable increase in thickness without damage to the fiber structure (2). The reasons for the choice of substrate, monomer, and redox system have been discussed in our previous paper (1). The properties that may be imparted to leather by the polymerization of other monomers in the chrome-tanned stock will be the subject of another publication in this series (3). In order to make this process economically feasible it was desirable to establish the optimum conditions for maximum polymer uptake. Unfortunately, very few studies of this nature have been conducted on proteins, particularly collagen. Rao and co-workers (4, 5) have reported the influence of various factors on the grafting of vinyl monomers onto collagen by ceric-ion initiation, while Wolfram and Menkart (6), Sugiyama (7), and Song *et al.* (8) have published their results of similar studies on wool and silk, respectively. None of this work was directly applicable to our research, however, since chrome-tanned hide substance, which was chosen as the substrate, is considerably different from these other proteins studied.

In this paper, the effects of a number of variables on the uptake of polymer by chrome-tanned substrate have been studied in detail in an attempt to find the optimum conditions for carrying out the graft polymerization on chrome-tanned Nigerian sheepskins.

EXPERIMENTAL

Chemicals and Materials

Butyl acrylate, containing five p.p.m. of the monomethyl ether of hydroquinone (MEHQ) as an inhibitor, was obtained from Rohm & Haas Company†. No attempt to remove this low level of inhibitor was made. The potassium persulfate was Fisher Scientific certified grade and the sodium bisulfite and the ethyl acetate were obtained from Eastman Kodak Company.

The various surfactants were obtained from a number of sources, as follows:

- 1) Triton X series — Rohm & Haas Company
- 2) Polyglycol E 6000 — Dow Chemical Company
- 3) Dowanol DPM — Dow Chemical Company
- 4) Carbowax 750 — Union Carbide Chemical Company
- 5) Tergitol series — Union Carbide Chemical Company
- 6) Ethomeen series — Armour Industrial Chemical Company
- 7) Ethofat 60/15 — Armour Industrial Chemical Company
- 8) Ethamid HT/15 — Armour Industrial Chemical Company

†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.

- 9) Span 60 — Atlas Chemical Company
- 10) Tween 40 — Atlas Chemical Company
- 11) Igepon series — GAF Corporation

Chrome-tanned Nigerian sheepskins used for these experiments were obtained from various tanneries. In the small scale experiments, eight-in. square pieces were run in the tumbling machine in tightly sealed two-quart Mason jars.

Graft Polymerization Procedure

The general graft polymerization procedure is outlined in Table I. This has been slightly modified since the publication of our previous paper (1). In addition

TABLE I
RECOMMENDED GRAFT POLYMERIZATION PROCEDURE

Blue Stock	100%
Water	200%
Initiator	
Potassium persulfate	1%
Sodium bisulfite	0.33%
Flush with CO ₂ , seal, and run for 1/2 hour.	
Monomer	Up to 25%
Surfactant	
Alkylphenoxy polyethoxy ethanol	1%
Flush with CO ₂ , seal, run for up to 24 hours.	

to an initiator time delay period of 1/2 hour, Triton X-100 (an alkylphenoxy polyethoxy ethanol) is now used instead of the surfactant mixture originally proposed. This basic formula was used in all subsequent experiments; however, the components were varied to study their effect on the uptake of polymer by the chrome-tanned substrate.

Analytical Determinations

The total nitrogen, moisture, and ash were determined as outlined in our previous publication (1).

Extraction of Homopolymer

Approximately 3.0 grams of the dried, ground product was weighed on the analytical balance, placed in a thimble, and extracted in a Soxhlet apparatus for 24 hours with ethyl acetate. This extract was taken to dryness on the steam bath and the residue was heated for an additional 24 hours at 100°C, cooled, and weighed. The general method and the calculations used were similar to those outlined in the A.I.C.A. Method B4 (9). A second extraction of the same sample

with fresh ethyl acetate for another 24 hours failed to remove more than one or two percent more homopolymer. A third extraction failed to remove any more material. The results presented here are based on a single extraction.

DISCUSSION AND RESULTS

In our graft polymerization treatments the amount of monomer added was based on the wet weight of the chrome-tanned sheepskin, which contained approximately 25 percent chrome-tanned hide substance. Thus, the use of 25 percent monomer would yield a product which was about 50 percent synthetic polymer on a dry basis, if all the monomer reacted. This we have called total polymer and have measured the amount present by total nitrogen (Kjeldahl) analyses. On extraction of the products with organic solvents, such as ethyl acetate, about half of the synthetic polymer could be removed as homopolymer. The remaining, nonextractable, synthetic polymer was presumably grafted to the collagen molecule. This we have called bound polymer.

One of the most important factors affecting the economics of the graft polymerization process is the amount of polymer necessary to give the desired improvement in the physical properties of the finished leather. To determine this, chrome-tanned Nigerian sheepskins were treated with increasing amounts of butyl acrylate ranging from 2.5 percent to 50 percent, based on the wet weight of the skin. The results are tabulated in Table II. As the amount of butyl acrylate added to the substrate was increased to 20 percent, essentially all the monomer

TABLE II
CHROME-TANNED NIGERIAN SHEEPSKIN TREATED WITH
INCREASING AMOUNTS OF BUTYL ACRYLATE (BA)

Exper. No.	% Persulfate Added*	% BA Added	% Total Polymer†	% Homopolymer‡	% Bound Polymer**
1	1.0	2.5	12	6	6
2	1.0	5.0	18	9	9
3	1.0	10.0	30	17	13
4	1.0	15.0	35	21	14
5	1.0	20.0	41	23	18
6	1.0	30.0	35	18	17
7	1.0	40.0	57	32	25
8	1.0	50.0	49	28	21
9	2.0	50.0	70	35	35

*Percentages of persulfate and monomer are based on the wet weight of the skin. Sodium bisulfite was added also in 1/3 the amount of the potassium persulfate.

†Percentages of total polymer are based on nitrogen determinations.

‡Determined by extraction with ethyl acetate.

**By difference.

was consumed and the yield of total polymer was close to quantitative. The products had the appearance of natural chrome-tanned stock. Above the 20 percent monomer addition level, erratic results were obtained. This was probably owing to the fact that above this level a one percent initiating system was not adequate. When the chrome-tanned substrate was treated with 50 percent butyl acrylate using a two percent initiator, a significant increase in the bound polymer to about 35 percent occurred and a quantitative yield of total polymer was again obtained. The treated leather had increased markedly in thickness and the deposition of polymer was evident through the entire cross section, as well as on the surfaces.

The optimal amount of butyl acrylate appears to be about 25 percent, based on the wet weight of the skin. In any case, at least ten percent monomer should be used to produce a noticeable effect. Below this level no desirable changes in physical properties were observed and the treated skins remained thin and somewhat brittle after drying. At concentrations above 25 percent a considerable amount of surface deposition occurred, giving the leather a tacky feel.

The amount of polymer formed in the collagen fibers was also dependent on the type of initiating system that was used. In our previous publication (1) we had established that a redox system consisting of potassium persulfate and sodium bisulfite in stoichiometric combination was most effective as a free-radical source for initiating the graft polymerization of butyl acrylate. To determine the optimum conditions for the deposition of polymer with this system, chrome-tanned

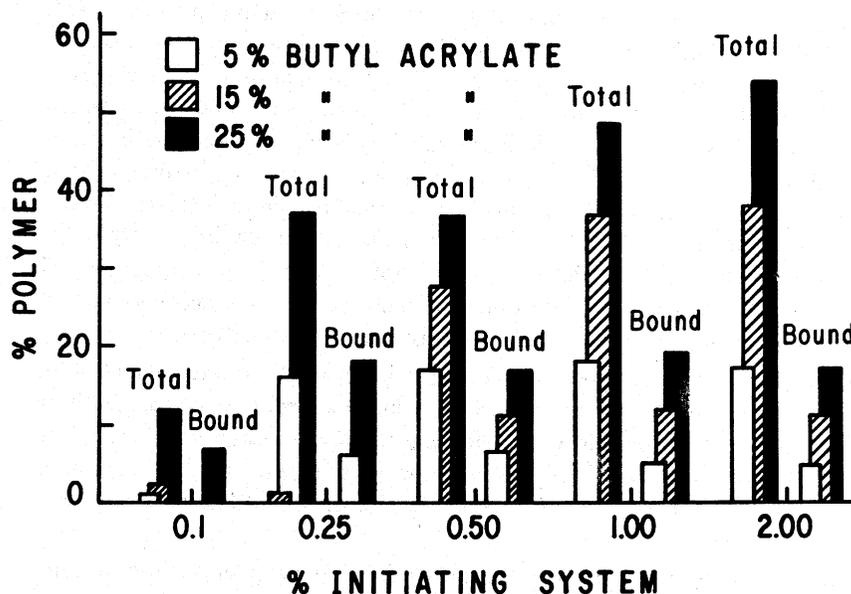


FIGURE 1.—Effect of amounts of initiating system on the uptake of butyl acrylate.

substrate was subjected to treatment with increasing amounts of the oxidizing and reducing agents at several monomer levels. The results are shown in Figure 1. At a concentration of five percent butyl acrylate, maximum polymerization was achieved when only 0.25 percent initiator was used, while one percent was required when 15 percent or 25 percent butyl acrylate was used. Inconsistent results were obtained with lower amounts of initiator. The optimal amount for this substrate, therefore, appears to be about one percent, based on the wet weight of the skin.

The use of various redox systems for initiating polymerization of acrylic monomers in collagen has not been extensively investigated. However, some work has been reported in the literature. Kudaba and Ciziunaite (10) used a ferrous ion-hydrogen peroxide system to graft vinyl monomers onto collagen, while Lipson and Speakman (11) used the same system for grafting acrylic acid and acrylonitrile onto wool. Deasy and co-workers (12) have established that certain metal-peroxide systems can attack collagen at room temperature and cause extensive degradation. Consequently, this redox system was not investigated. Simpson *et al.* (13) employed silver persulfate and Negishi and co-workers (14) used sodium persulfate and lithium bromide to polymerize various acrylates onto wool.

A number of redox systems were investigated at our laboratory involving the use of potassium persulfate in combination with a variety of reducing agents in the absence and presence of air. The maximum yield of polymer possible in this study was 23 percent. As shown in Table III, the potassium persulfate-silver nitrate system resulted in the maximum formation of bound poly(butyl acrylate). Unfortunately, the final product was discolored. The grayish-purple appearance was due to the interaction of the silver nitrate with protein and to the exposure to light. While the use of sodium bisulfite resulted in the formation of less bound polymer than with silver nitrate, the appearance and the physical properties of the final product were superior. The other reducing agents, ferrous sulfate, sodium dithionite, lithium bromide, and sodium formaldehyde sulfoxylate, showed a marked decrease in effectiveness. The potassium persulfate/lithium bromide redox system showed the same ability to initiate the graft polymerization of butyl acrylate in air as under carbon dioxide and most of the polymer was bound. However, only 25 percent of the monomer was converted to polymer.

Since butyl acrylate and other acrylic esters have only a limited water solubility, any means of dispersing these monomers in an aqueous system to facilitate penetration into the hide or skin would be of great practical significance. Surface active agents have been used for this purpose in the graft polymerization of proteins by many workers (15, 16), and this aqueous emulsion technique was applied to our process.

To establish the level of surfactant required for maximum deposition of polymer, a series of chrome-tanned sheepskin samples were treated with increasing amounts of an efficient non-ionic wetting agent, Triton X-100. Surprisingly, the

TABLE III

EFFECT OF VARIOUS REDOX SYSTEMS ON THE UPTAKE OF BUTYL ACRYLATE BY CHROME-TANNED NIGERIAN SHEEPSKIN

Exper. No.	Redox System	Atmos.	% Total Polymer†	% Homo-polymer‡	% Bound Polymer**
1	K persulfate — Na bisulfite	CO ₂	23	13	10
2	" — Formopon*	"	4	1	3
3	" — silver nitrate	"	21	3	18
4	" — Na dithionite	"	14	7	7
5	" — Na bisulfite - Fe sulfate	"	22	13	9
6	" — lithium bromide	"	6	1	5
7	" — Na bisulfite	Air	3	1	2
8	" — Formopon*	"	1	1	0
9	" — silver nitrate	"	1	1	0
10	" — Na dithionite	"	2	1	1
11	" — Na bisulfite - Fe sulfate	"	4	1	3
12	" — lithium bromide	"	6	1	5

*Formopon = sodium formaldehyde sulfoxylate.

†Percentages based on nitrogen determinations — maximum possible, 23 percent polymer.

‡Determined by extraction with ethyl acetate.

**By difference.

results showed that, with 25 percent butyl acrylate, no significant difference in the uptake of bound polymer was observed over the range of concentrations of Triton X-100 from 0.0 to 2.0 percent.

Since it was known that Triton X-100 did affect the polymerization of other acrylates (17), various types of surfactants were tested for their effect on the degree of polymerization of butyl acrylate. One percent of the wetting agent was used and in most cases gave a satisfactory emulsion when thoroughly mixed with as much as 25 percent monomer. These percentages are based on the wet weight of the substrate. The results obtained with the most effective surfactants are given in Table IV. As a class, nonionic and anionic surfactants, either alone or in a 1:1 mixture, gave the best results. Cationic wetting agents generally gave poor results; however, Ethomeen T-15 was fair. In view of these results, we recommend using about one percent of one of the better surfactants in Table IV or a comparable product.

It has been reported by various workers that pH affects the rate of graft polymerization. Rao (18) found that the optimum pH for grafting vinyl monomers onto untanned collagen was 2.1 when using ceric ion initiators, while Simpson and van Pelt (13) observed that for wool few polymerization reactions can be carried out below pH 5. In our work with a persulfate-bisulfite redox

system, using chrome-tanned substrate and a 25 percent butyl acrylate concentration at pH ranges from 2 to 6, we found that the high buffering capacity of this system caused the final pH values to approach 4. Since this was the pH of most chrome-tanned stock, no adjustments of pH were necessary. At this pH the graft polymerization proceeded in a satisfactory manner, in most cases with complete monomer exhaustion.

The effect that the length of the delay in the addition of butyl acrylate had on the uptake of polymer is summarized in Table V. No significant increase in

TABLE IV
EFFECT OF VARIOUS SURFACTANTS ON THE GRAFT POLYMERIZATION OF BUTYL ACRYLATE ONTO CHROME-TANNED NIGERIAN SHEEPSKIN

Exper. No.	Surfactant	Type	% Total Polymer*	% Homo-polymer†	% Bound Polymer‡
1	Triton X-45	Non-ionic	53	29	24
2	" X-100	" "	48	27	21
3	" X-155	" "	49	29	20
4	" X-305	" "	30	17	13
5	" X-405	" "	35	20	15
6	" X-700	" "	38	22	16
7	Ethomeen T-15	Cationic	44	31	13
8	Tween 40	Non-ionic	46	27	19
9	Igepon T-77	Anionic	38	23	15
10	GAFAC RE 610	"	50	32	18

*Based on nitrogen determinations.

†Determined by extraction with ethyl acetate.

‡By difference.

TABLE V
TREATMENT OF CHROME-TANNED NIGERIAN SHEEPSKIN WITH PRE-EMULSIFIED BUTYL ACRYLATE (BA)

Exper. No.	Delay Before Adding BA (hours)	% Total Polymer*	% Homo-polymer†	% Bound Polymer‡
1	0	50	35	15
2	1/2	55	31	24
3	1	41	22	19
4	2	33	16	17
5	4	34	18	16

*Percentages of total polymer based on nitrogen determination.

†Determined by extraction with ethyl acetate.

‡By difference.

TABLE VI
EFFECT OF THE SEQUENCE OF ADDITION ON THE GRAFT POLYMERIZATION OF BUTYL ACRYLATE (BA)

Exper. No.	Added Initially	Atmos.	Added After ½ Hour	% Total Polymer*	% Homo-polymer†	% Bound Polymer‡
1	Monomer, surfactant, persulfate, bisulfite	CO ₂	—	54	32	22
2	Persulfate	"	Monomer, surfactant, bisulfite	58	38	20
3	Persulfate, bisulfite	"	Monomer, surfactant	55	34	21
4	Monomer, surfactant, persulfate	"	Bisulfite	52	35	17
5	Monomer, surfactant	"	Persulfate, bisulfite	53	36	17
6	Monomer, surfactant, bisulfite	"	Persulfate	57	38	19
7	Monomer, surfactant, persulfate, bisulfite	Air	CO ₂	51	23	28
8	Persulfate	"	Monomer, surfactant, bisulfite, CO ₂	56	35	21
9	Persulfate, bisulfite	"	Monomer, surfactant, CO ₂	56	32	24
10	Monomer, surfactant, persulfate	"	Bisulfite, CO ₂	57	37	20
11	Monomer, surfactant	"	Persulfate, bisulfite, CO ₂	54	34	20
12	Monomer, surfactant, bisulfite	"	Persulfate, CO ₂	55	37	18

*Based on nitrogen determinations.

†Determined by extraction with ethyl acetate.

‡By difference.

bound polymer was observed when the monomer was emulsified in a blender before being added to the polymerization mixture. However, a marked increase was noted when the initiator was tumbled with the skin for $\frac{1}{2}$ hour before the addition of the pre-emulsified monomer. Longer time delays for periods up to four hours were less successful, probably owing to the slow destruction of the free radicals by side reactions. Both the total and bound polymer contents were formed at maximum levels after the $\frac{1}{2}$ hour delay.

In Table VI the effect that the sequence of addition of the various components had on the graft polymerization is shown. All experiments in this series resulted in essentially quantitative yields of total polymer. There were some small differences in the yields of bound polymer, however. Allowing all of the reagents to react with the substrate for $\frac{1}{2}$ hour in the presence of air before adding the CO_2 (Experiment 7) gave the highest yield. Addition of the persulfate and bisulfite alone in air, followed by addition of the monomer, surfactant, and CO_2 $\frac{1}{2}$ hour later (Experiment 9), gave fair results, as did the two comparable sequences done completely under CO_2 (Experiments 1 and 3). When the monomer was added before the persulfate, bisulfite, or both under CO_2 (Experiments 4, 5, and 6), a decrease in the amount of bound polymer resulted and there was considerable surface deposition of polymer, which resulted in a tacky product. In comparable sequences started under air (Experiments 10, 11, and 12) this did not happen. The indications are that, for good results, the initiating system must be allowed to react with the hide or skin for a short period of time before polymerization starts or the yield of bound polymer is poor and surface deposition of homopolymer occurs. In view of this and for the sake of convenience, we recommend adding the initiating system with the hides or skins and float and flushing the container with CO_2 . The monomer can be added later and the surfactant can be added at either time.

TABLE VII
EFFECT OF TIME ON THE UPTAKE OF BUTYL ACRYLATE
BY CHROME-TANNED NIGERIAN SHEEPSKIN

Exper. No.	Reaction Time* (hours)	% Total Polymer†	% Homo-polymer‡	% Bound Polymer**
1	1	29	18	11
2	2	41	29	12
3	4	46	31	15
4	8	49	31	18
5	24	52	33	19

*After $\frac{1}{2}$ hour delay.

†Based on nitrogen determinations.

‡Determined by extraction with ethyl acetate.

**By difference.

An important consideration in this process to tanners would be the length of time required to achieve maximum graft polymerization. Accordingly, polymerizations were stopped after various times up to 24 hours and the results are summarized in Table VII. Based on total nitrogen analyses, the butyl acrylate was completely polymerized after eight hours at the 25 percent level, although, on visual examination of the spent liquors, the monomer appears to be completely exhausted after four hours. For lesser amounts of monomer, a shorter time may be possible; but, for this amount (25 percent), at least eight hours is required.

To determine the uniformity of polymer distribution, an entire chrome-tanned skin was treated with butyl acrylate at a 25 percent concentration and the degree of graft polymerization was measured at standard locations, as indicated in Figure 2. The total uptake of poly(butyl acrylate) ranges from 49 to 57 percent in the flanks or belly area and from 42 to 47 percent in the neck and backbone regions. The loose corium structure of the belly area would be expected to facilitate the diffusion of monomer into the protein fibers, while the more compact areas in the neck and backbone would be more resistant. Although there was this significant variation in the amount of the total polymer, little difference was observed in the amount of bound polymer, which is directly dependent on the amount of hide substance present and therefore would be uniform over the whole

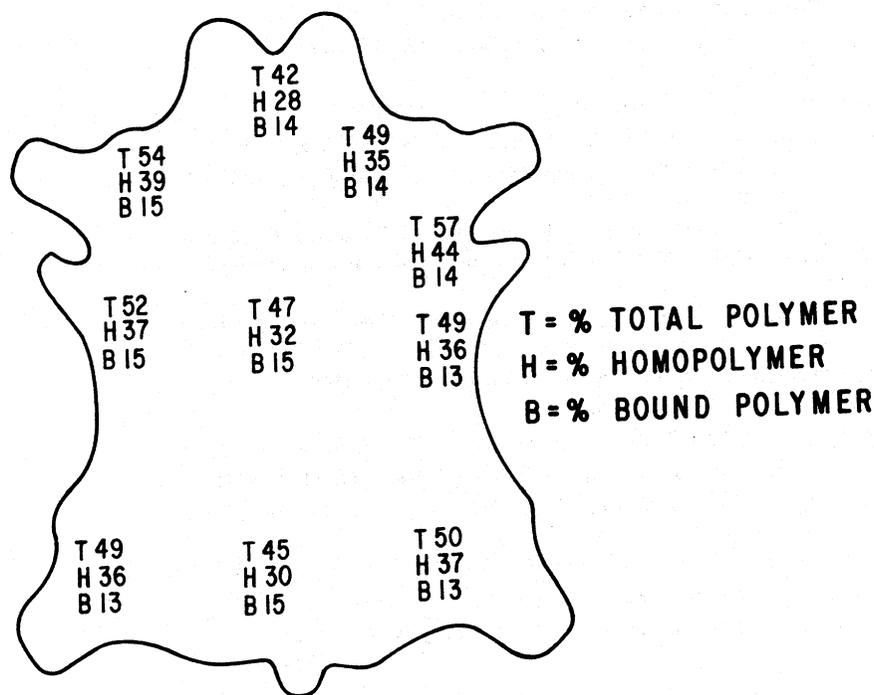


FIGURE 2.—Distribution of poly(butyl acrylate).

skin. These results suggest that this might afford an excellent way of filling out and upgrading the thin belly sections so that they might be of more commercial importance.

In summary, our work on establishing the optimum conditions for conducting the graft polymerization of acrylic esters indicates that this process should be carried out for at least eight hours (using a 25 percent concentration of monomer based on the blue weight) with one percent nonionic surfactant, such as Triton X-100, one percent potassium persulfate, and 0.33 percent sodium bisulfite, using a 200 percent float and dry ice to exclude air from the drum. It is desirable to add the persulfate and bisulfite $\frac{1}{2}$ hour before the addition of the other ingredients and, perhaps, to add the monomer in an emulsified form. The CO₂ can be added initially or with the monomer, whichever is more convenient. In any case, the redox system must be allowed to react with the skin for about one half hour before adding the monomer.

REFERENCES

1. Korn, A. H., Fearheller, S. H., and Filachione, E. M. *JALCA*, **67**, 111 (1972).
2. Mellon, E. F. "Encyclopedia of Polymer Science and Technology," Vol. 8, p. 195, John Wiley & Sons, Inc., New York, N. Y., 1968.
3. Harris, E. H., Jr., Taylor, M. M., and Fearheller, S. H. *JALCA* (in press).
4. Rao, K. P., Joseph, K. T., and Nayudamma, Y. *Das Leder*, **19**, 77 (1968).
5. Rao, K. P. *Leather Sci.*, **15**, 92 (1968).
6. Wolfram, L. J., and Menkart, J. *Am. Dyestuff Reporter*, **56**, 110 (1967).
7. Sugiyama, H., and Murase, R. *Bull. Textile Research Inst. Japan*, **70**, 34 (1965).
8. Song, T. O., Kim, Y. D., and Noh, I. S. *Kungnip Kongop Yonguso Pogo*, **16**, 7 (1966) (Korean); *Chem. Abstracts*, **69**, 11312d (1968).
9. Official Methods of Analysis, ALCA, 1953. May be secured from the Secretary-Treasurer of ALCA, Tanners' Council Research Laboratory, University of Cincinnati, Cincinnati, Ohio 45221.
10. Kudaba, J., and Ciziunaite, E. *Liet. TSR Aukst. Mokyklu. Mokslo Darb., Chem. Chem. Technol.*, **9**, 167 (1969) (Lithuanian); *Chem. Abstracts*, **72**, 32428y (1970).
11. Lipson, M., and Speakman, J. B. *J. Soc. Dyers Colourists*, **65**, 390 (1949).
12. Deasy, C., and Ernst, E. *JALCA*, **64**, 345 (1969).
13. Simpson, W. S., and van Pelt, W. *J. Text. Inst. Trans.*, **57**, T493 (1966).
14. Negishi, M., Arai, K., and Okada, S. *J. Applied Polymer Science*, **11**, 115 (1967).
15. Ishibashi, H., and Oku, M. *Proc. Int. Wool Text. Res. Conf.*, Vol. 3, (Sect. III), p. 377, 1965.
16. Jackson, D. L. C. *Textile Research J.*, **24**, 624 (1954).
17. Unpublished results, manuscript in preparation.
18. Rao, K. P., Joseph, K. T., and Nayudamma, Y. *Leather Sci.*, **19**, 27 (1972).

DISCUSSION

MR. HAYWOOD G. FRANCE (Union Carbide Corp.): I would like to thank Mr. Korn for the excellent presentation of the second in a series of papers covering some very interesting work being done in his laboratory. Certainly the new type technique of a drum impregnation has wide interest for all of us. Based on the enthusiasm and the interest shown in the first paper given in this series last year, I would like to ask for questions from the floor at this time. For accuracy in transcription, will the persons having questions please go to one of the aisle microphones and state their names and companies prior to addressing their questions to Mr. Korn? Do we have any questions from the floor?

I have one, Al, to start the discussion. Toward the end of your talk you discussed the impregnation of polymer, where you said the bound polymer was directly related to the hide substance. This would indicate that this is due to some specific grafting site that is occurring in the hide substance. Has any work been done in this area?

MR. A. H. KORN: You are referring, of course, to the mechanism that is involved. Yes, we have done some preliminary work in this direction. We carried out some amino acid analyses on some of the hydrolyzed treated material. We discovered that certain amino acids, such as tyrosine and the other hydroxyamino acids, were greatly reduced after treatment of the leather. However, these amino acids occur in such small amounts that this factor cannot possibly account for all of the polymer that is taken up. Thus we believe that there are additional sites of attachment, probably the peptide group. We are in the process now of trying to separate some of these grafted materials by hydrolysis to see if we can get any further information in this direction.

DR. LUDWIG SELIGSBERGER (U.S. Army Natick Laboratories): First, did I understand correctly that treatment should be continued for at least twenty-four hours? Do you mean that drumming is stopped and the reaction would still proceed in the skins for another 20 hours to reach the maximum? Or do you mean that it is necessary to proceed with continuous drumming to obtain the maximum reaction which would be sure to have occurred after 24 hours or so? I am concerned with the energy input and with the fact that in other reactions we have a possibility of horsing up the skins and not touching them for 24 to 48 hours, believing that there will be additional fixation this way.

Second, I believe you said ethyl acetate was used for extraction. What would happen if you used the normal officially approved extraction solvents, like chloroform or normal hexane, with which the ALCA-ASTM Joint Committee is now working?

MR. KORN: To answer the first part of your question, we started with a 24-hour period of reaction initially. We discovered later that only eight hours of reaction would be sufficient, and perhaps four hours. I would say that if the

reaction were carried out between four and eight hours, certainly as much monomer as the system will contain would be incorporated. Regarding the second part of your question, we haven't tried chloroform for extraction. It would probably do a fairly good job, but I think ethyl acetate would be better. Ethyl acetate is one of the solvents that is officially recommended for the removal of homopolymer. This is the reason for our use of the ethyl acetate. There are other solvents but they are rather volatile and rather dangerous, so we continued to use ethyl acetate.

DR. PETER R. BUECHLER (K. J. Quinn and Co.): It is probably in your paper, but I don't recall in the presentation that you discussed the amount of exotherm here. Perhaps this was given in your earlier paper. What kind of temperatures are reached with the formulation system that you have when there are 200 parts of water to 100 parts of blue stock, plus the other ingredients?

MR. KORN: To the best of our knowledge, the temperatures do not go much above room temperature. We haven't made a really accurate study of this factor but we have never observed an appreciable amount of heating.

DR. BUECHLER: This is rather surprising because a redox polymerization is usually quite exothermic.

MR. KORN: This may be so, but we have not observed any amount of heating. We may try to determine that more closely in the future.

MR. FRANCE: Are there any further questions? To keep on with our schedule, then—Al, I want to again thank you and express our appreciation to you and your co-workers for the excellent work that you are doing in this area.
