LEATHER-FIBER LUBRICANT RESISTANT TO REMOVAL BY DRYCLEANING SOLVENTS. III. LONG-CHAIN *N*-SUBSTITUTED AMPHOTERIC BETAINES*

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ABSTRACT

This report describes the evaluation of a series of long-chain *N*-substituted betaine amphoteric compounds ($RN^+(CH_3)_2CH_2COO^-$) as leather-fiber lubricants in place of conventional fatliquors from the standpoint of resistance to drycleaning solvents. The data presented show these compounds resist removal from the leather by common drycleaning agents — Stoddard solvent, perchloroethylene, and 1,1,2-trichloro-1,2,2-trifluoroethane. Laboratory tests were run on small leather pieces, and simulated commercial tests were also run on whole skins. The compounds are available commercially under the trade name "Lonzaine"‡**.

INTRODUCTION

Two previous papers (1, 2) from our laboratory reported studies on the use of novel substances as leather-fiber lubricants. These substances were amphoteric surfactants which were available under the trade name "Deriphat"†† and were *N*-substituted fatty derivatives of β-aminopropionic acid of the general formula $RNHCH_2CH_2COOM$, where R is a long chain hydrocarbon radical and M is hydrogen or a metal cation. Our interest stemmed from the fact that these compounds were suggested for application in cosmetics because of their substantivity to protein substrates. Our results indicated these materials were substantive to leather fiber and provided lubrication. Furthermore, fiber lubrication with these amphoteric materials resulted in leathers that resisted removal of lubricant by most of the commonly used drycleaning solvents.

*Presented in part at the 70th Annual Meeting of the American Leather Chemists Association, Pocono Manor, Penna., June 16–19, 1974.

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

‡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.

**A series of Lonzaines are available from Lonza, Inc., Fairlawn, N. J. 07410.

††A series of compounds available from the Chemical Division, General Mills, Inc., Minneapolis, Minn. 55435.

Another series of amphoteric surfactants, known under the trade name "Lonzaine," has also become available recently. These are long chain *N*-substituted betaines of the general structure $RN^{+}(CH_3)_2CH_2CO_2^{-}$, where R is a long chain alkyl group. Unlike the Deriphats, the nitrogen in the betaine series of compounds is a quaternary type and thus is a stronger base. These betaines are "stable" in neutral systems, are biodegradable, and have been stated to exhibit substantivity to both skin and hair and have excellent foaming ability in both hard and soft water.

Because of their zwitterion character, these long chain amino acid derivatives, Deriphats as well as Lonzaines, exhibit both a cationic and an anionic nature. They would therefore be expected to show substantivity to charged substrates (for example, chrome-tanned collagen which is cationic) through electrostatic forces. We may further speculate that these amino acid derivatives may show substantivity to chrome leather through co-ordination with chrome in the chrome-collagen complex. Since the Lonzaines, like the Deriphats, are long chain amphoteric surfactants, we have evaluated these substituted betaines as potential leather lubricants resistant to removal by drycleaning.

EXPERIMENTAL

This section is divided as follows. Part A is concerned with the tannage of the leather used in the experimental work and with the fiber lubricants under test. The work described in Part A is common to the experimental work described in Parts B and C. Part B is concerned with the work done in our laboratory on small pieces of leather. Part C outlines the work done on full skins in cooperation with a tanner and commercial drycleaners.

Part A — Experimental Skins and Fiber Lubricating Agents

1. Retannage of Chrome-Tanned Skins with Glutaraldehyde. Glutaraldehyde retannage was selected to provide the leathers for the experimental work. Wet, chrome-tanned garment suede skins were obtained from a tanner who removed them from the tanning drum after neutralization and just before the fatliquoring step of his commercial process. The skins were retanned in our laboratory in a small tanning drum (24 in. diameter and 12 in. wide) with glutaraldehyde (25 percent aqueous solution) at 50°C., using ten percent of the wrung, blue weight of the skins, in a 100 percent float at a pH range of 3.1 to 3.5 for six hrs. (3, 4). The skins were then washed in running water to remove unused glutaraldehyde, wrung, packed in polyethylene bags, and refrigerated to await further treatment. The shrinkage temperatures (determined in water under pressure (5)) were essentially the same as those for the chrome-tanned skins that were not retanned (116 $\pm$ 2°C.).

2. Amphoteric, N-Substituted Betaines (6). The series of compounds listed and described in Tables I and II are the Lonzaine materials evaluated as poten-

TABLE I

COMPOSITION OF VARIOUS COMMERCIAL BETAINES, $RN^+ CH_3)_2CH_2COO^-$ (6a)

Lonzaine	Alkyl Group	Alkyl Group Distribution (%)				
		C_{10}	C_{12}	C_{14}	C_{16}	C_{18}
10S	Decyl	95 min.				
12C	Coco	8	46	24	10	7 max.
14	Mixed		40	50	10	
16S	Cetyl				95	
18S	Stearyl					95 min.

TABLE II

PROPERTIES OF VARIOUS COMMERCIAL BETAINES (6a)

Property	Light Yellow Free Flowing Liquid				Pearlescent Free Flowing Liquid
	10S	12C	14	16S	18S
Percent active	41.0	32.0	31.0	31.0	31.0
Percent NaCl	2.5	1.5	1.5	1.0	0.5
Solvent	H_2O	H_2O	H_2O	Water/ Ethanol*	Water/ Ethanol*
pH (10 percent solution)	7.2	7.5	7.25	7.5	7.4

*Ten percent ethanol — balance water.

tial drycleanable leather fiber lubricants. The major chain-length (R) distribution of the commercial products used shows the typical composition of each product.

Part B — Laboratory Tests on Small Leather Samples

1. *Removal of Natural Fat and Other Soluble Materials from Samples.* To produce a supply of leather samples for treatment and subsequent analysis, several chrome, glutaraldehyde-retanned skins described in Part A above were cut and preextracted as follows. The skins were cut into three in. by ten in. pieces, the longer dimension at right angles to the backbone. The flanks and ends were discarded. The pieces were spread in a shallow covered pan and immersed in acetone. The extractions with acetone were followed by Soxhlet extractions for seven hrs. each with chloroform and 95 percent ethyl alcohol. The samples were then air-dried and finally dried in a vacuum oven at 50°C. at a pressure of five to ten mm. Hg for 48 hrs. The moisture-free weight of each piece was recorded for use in future calculations (2).

2. *Lubrication of Test Pieces with Betaine Amphoteric Compounds.* The test pieces of leather, as prepared in B-1 above, were wet-back in water and then passed through a wringer. Based on the wet-weight (w.w.) of the pieces used, they were placed in jars containing 15 percent (w.w.) betaine amphoteric solution as received††, 50 percent (w.w.) water, and two drops of Dow-Corning anti-foam Reagent B. The mixture was warmed to 50°C. and tumbled for ten min. Ten ml. water was then added and tumbling continued for 1.5 hrs. A heat lamp was used to maintain the temperature at 50°C. The leather pieces were then drained and allowed to air-dry overnight. The samples were then dried at 50°C. for 48 hrs. in a vacuum oven (five to ten mm. Hg). The samples were cooled over desiccant and weighed to obtain uptake of lubricant.

3. *Treatment of Leather Pieces Containing Fiber Lubricant with Drycleaning Solvents.* Three leather pieces, as prepared above, weighing 25 to 30 grams each were placed in a jar containing 400 ml. of the drycleaning solvent (Stoddard, Valclene, or perchloroethylene). The jar was tumbled at 44 r.p.m. at room temperature for 30 min. The leather pieces were removed from the jar, and allowed to air-dry. The samples were then dried at 50°C. in a vacuum oven at five to ten mm. Hg for 48 hrs.

Part C — Laboratory Tests on Full Suede Skins

1. *Treatment of Suede Skins with Betaine Amphoteric Compounds.* Chrome-glutaraldehyde retanned skins, prepared as described earlier under Part A of the Experimental Section, were selected for treatment with the Lonzaine materials listed. Small pieces of leather from each skin were removed for determination of natural fat by extraction with 95 percent ethyl alcohol. Skin #1 was treated in a solution comprising 50 percent (w.w.) water and 15 percent Lonzaine 14. The solution was preheated in a small laboratory drum to 50°C. The skin was tumbled in this solution for 1.5 hrs. (pH = 4.1), removed from the drum, hand squeezed, placed in a polyethylene bag, and refrigerated to await further processing.

Skin #2 was treated in a similar manner with Lonzaine 12C and Skin #4 with Lonzaine 10S; Skin #5 and Skin #3 were treated essentially as above in a solution obtained from 50 percent (on wet weight) of ethanol-water (nine parts water, one part ethanol), and 15 percent (on wet weight) of Lonzaine 18S and Lonzaine 16S, respectively. Aqueous ethanol was used because of the limited solubility of these two betaines. There was very little change in shrinkage temperature of these skins after the treatments listed.

These skins were sent to a tannery, where they were dried and processed (with no additional fatliquor) into suede garment leather. Skin #6, which had not been treated with a Lonzaine, was sent along with the others for processing into brown suede leather using the conventional tannery fatliquor for purposes of

‡‡For example, Lonzaine 14 is supplied as a 32 percent solution.

comparison. The finished leathers were all of good, commercial appearance and quality, and level in color. The shrinkage temperatures were unchanged, except for the skin treated with Lonzaine 10S, which dropped several degrees.

2. *Sampling Leather for Drycleaning Tests.* Ten in. by ten in. pieces of leather were cut from each of the six skins described in Part C-1 above. All samples were taken from the central portion of the skin. The flanks, neck, and tail portions were discarded. Strips of leather from between the squares were used for analyses of the leather for "before drycleaning" data. Each piece of leather was stamped for identification and stapled to a towel which helped make up the load for the drycleaning cycle. The drycleaning was done in commercial equipment with a dummy load.

3. *Drycleaning Tests.* Leather from each of the six skins described in Part C above were drycleaned twice in Stoddard solvent (a petroleum fraction containing no drycleaning detergents or soap) by a local leather-drycleaning specialist.

Other pieces of leather from each skin were drycleaned twice with Valclene (1,1,2-trichloro-1,2,2-trifluoroethane) in a "coin-op" machine especially designed to use this solvent by the DuPont Dry-Cleaning Products Laboratory.

The remaining leather from each skin was drycleaned twice by the laboratory of the International Fabricare Institute*** in standard equipment, using perchloroethylene containing some drycleaning detergent (about one third that normally used in drycleaning clothing).

TABLE III

EFFECT OF TIME ON EXTRACTION OF BETAINE AMPHOTERIC FIBER LUBRICANT (LONZAINE 14) FROM LEATHER BY 95 PERCENT ETHYL ALCOHOL

Sample	Time (Hours)	Betaine Amphoteric Compounds* (%)	
		In Leather†	Extracted
1	7	10.13	10.94
2	14	10.37	10.98

*Lonzaine 14; see Experimental Section, Part A.
†Calculated from gain in weight of treated samples; see Experimental Section, Part B.

After the leather samples had been drycleaned, they were returned to our laboratory for analysis of retained fiber lubricant. The method of analysis was essentially that described previously for Deriphat lubricated leathers (2). The amount of alcohol extractables was a measure of the lubricant content of the leathers.

***Drycleaning Division, 909 Burlington Ave., Silver Spring, Md. 20910.

Preliminary data, summarized in Table III, showed that a seven-hr. extraction with 95 percent ethyl alcohol was equivalent to the 14-hr. alcohol extraction previously used (2).

Additional leather samples from Skin #6, treated with a standard fatliquor, were also extracted with chloroform according to the ALCA Standard Method (Provisional) (7) for comparison with 95 percent ethyl alcohol extractions.

RESULTS AND DISCUSSION

1. Evaluation as Leather-Fiber Lubricants. All leathers treated with the Lonzaines instead of conventional fatliquors were of acceptable commercial quality and appeared to have adequate strength when tested qualitatively. The dyed leathers appeared uniformly colored. The leathers were soft and supple. They retained these desirable garment leather characteristics after drycleaning with the various drycleaning solvents. Incorporation of the Lonzaines did not lower the shrinkage temperature of the leather, an indication that crosslinkage of the tannage was not affected. Similar results were observed in our earlier studies using Deriphats as the leather fiber lubricant (1, 2).

2. Laboratory Extraction Studies. As shown in Table IV, no significant losses in weight were observed in any of the small retanned skin samples tested after 30 min. of tumbling in three common types of commercial drycleaning solvents, Valclene, Stoddard solvent, or perchloroethylene. This contact time is at least three times longer than that used in the normal drycleaning cycle and indicates the substantivity and excellent solvent-resistance of all five Lonzaines tested.

3. Commercial Drycleaning — Full Skin Tests. Table V presents data showing the amount of lubricant or fatty material, determined as alcohol extractables, retained in the leather after two drycleaning cycles in commercial type equipment. The natural fat content of these skins is also shown. There was some loss of lubricant or fatty material when Valclene or Stoddard solvent was used as drycleaning solvent. However, loss of lubricant was appreciably less than for the leather given the conventional fatliquor. In these full skin tests, however, the skins contained 4.0 to 5.5 percent natural fat, which is not resistant to removal by drycleaning solvents and complicates the analysis for lubricant in leathers.

Our studies with leathers from which the natural fat was first removed by solvent extraction before treatment with the Lonzaines (Table IV) clearly show little or no loss of lubricant on drycleaning with the three common types of drycleaning solvents. This supports our hypothesis that the losses on drycleaning in the full skin tests are losses of natural fat. Previous studies with the Deriphats, which are also amphoteric lubricants, also showed little loss of lubricant when the skins were defatted prior to lubrication (2).

TABLE IV

EFFECT OF DRYCLEANING SOLVENTS ON LEATHER PIECES LUBRICATED WITH BETAINE AMPHOTERIC COMPOUNDS

	Wt. of Leather Sample (MFB*)		
Fiber Lubricant	Before Drycleaning (g.)	After Drycleaning (g.)	Drycleaning Solvent
Lonzaine 10S	7.75	7.77	Valclene**
" 12C	7.97	7.97	"
" 12C	8.89	8.83	"
" 14	6.64	6.64	"
" 14	8.06	8.03	"
" 16S	8.48	8.43	"
" 18S	8.99	8.87	"
" 18S	9.11	9.08	"
" 10S	8.10	8.10	Stoddard†
" 12C	7.97	7.85	"
" 14	7.11	7.05	"
" 14	7.32	7.40	"
" 16S	9.13	8.99	"
" 18S	11.12	10.92	"
" 10S	7.60	7.56	Perchloroethylene
" 12C	8.69	8.53	"
" 14	6.23	6.20	"
" 14	9.06	8.97	"
" 16S	9.93	9.73	"
" 18S	11.40	11.24	"

*MFB = Moisture-free basis.

**Trade name of E. I. Dupont commercial drycleaning agent, (1,1,2-trichloro-1,2,2-trifluoroethane).

†Petroleum-base solvent specially refined for drycleaning (Specifications by U. S. Department of Commerce); white spirits.

As noted in Table V, drycleaning with perchloroethylene which contained a drycleaning detergent gave anomalous results. There was a slight increase in extractables upon drycleaning with this system, even though we would at least expect a loss of the natural fat to perchloroethylene, an excellent fat solvent. These results are probably due to the drycleaning detergent (present in the perchloroethylene) which is picked up by the leather. The uptake of detergent appears to offset extraction of any fat by the perchloroethylene. As seen in Table V, even the leathers with commercial fatliquors showed little apparent loss of lubricant with this drycleaning system despite the well known fact that convenional fatliquors are not resistant to removal by drycleaning.

Comparison of the data in Table V obtained using a standard chloroform extraction with those using the special seven-hr. 95 percent ethanol extraction de-

TABLE V

EFFECT OF TWO DRYCLEANING CYCLES ON ETHYL ALCOHOL (95%) EXTRACTABLES* FROM COMMERCIAL-TYPE SUEDE GARMENT LEATHER TREATED WITH BETAINE AMPHOTERIC COMPOUNDS AS LEATHER-FIBER LUBRICANTS

	Percent† Extracted by 95 Percent Ethyl Alcohol in Seven Hours of Skins Treated with Betaine Amphoteric Compounds				
			After Two Drycleaning Cycles with:		
Skin Number and Betaine Amphoteric Compounds‡ Applied	Natural Fats	Before Drycleaning	Valclene**	Stoddard Solvent††	Perchloro-ethylene and Drycleaning Detergent
Skin #1; (Lonzaine 14)‡	4.65	10.61	8.84	8.33	10.11
Skin #2; (Lonzaine 12C)‡	5.38	11.76	9.90	9.80	12.16
Skin #3; (Lonzaine 18S)‡	5.50	13.67	11.51	10.00	13.75
Skin #4; (Lonzaine 10S)‡	5.57	6.86	5.38	5.40	8.54
Skin #5; (Lonzaine 16S)‡	4.35	12.53	10.58	9.96	13.25
Skin #6; Commercial Fatliquor	5.14	9.25	5.68	5.10	8.79
	Percent Extracted by Chloroform‡‡				
Skin #6; Commercial Fatliquor	4.02	6.03	2.28	1.93	5.66

*Soxhlet extraction.

†Based on moisture-free weight of leather (MFB).

‡Trade names of betaine amphoteric compounds (see Experimental Section, Part A) available from Lonza, Inc., Fairlawn, N. J. 07410.

**Trade name of E. I. Dupont drycleaning agent (1,1,2-trichloro-1,2,2-trifluoro-ethane).

††Petroleum-base solvent specially refined for drycleaning (Specifications by U. S. Department of Commerce); similar to "white spirits."

‡‡ALCA Provisional Method; see Reference 7.

veloped especially for the Lonziane fatliquors, shows that essentially the same decreases in percent extractables are obtained in all three solvents by both methods when applied to Skin #6 processed with a conventional fatliquor, even though the total amounts extracted are appreciably different.

CONCLUSIONS

The experimental results reported indicate that the long chain, *N*-substituted betaine amphoteric compounds (as represented by the series of Lonzaines) evaluated in this paper are worthy of consideration as potential leather-fiber lubricants — fiber lubricants that are resistant to removal from the leather by the three most common drycleaning agents. Properly made garments of such leather should be drycleanable in "coin-op" machines, as well as by professional drycleaners.

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Received January 13, 1975.

DISCUSSION

MRS. JEAN TANCOUS (Tanners' Council Research Laboratory): The slogan "better products through chemistry" certainly applies to this work. We are grateful to Mr. Viola and his associates for this very excellent paper. The discussion leader for this paper will be Dr. Thorstensen.

DR. THOMAS THORSTENSEN (Thorstensen Laboratory): We should thank Sam and the Department of Agriculture. Once again the Department has brought in a new material with potential value to the leather industry. Of course, there is a big step between the initial work that Sam is doing and the eventual commercial application, which will require considerable additional work by the tanners who can apply this work.

I have one question. Sam, as we all know, glutaraldehyde has a strong softening effect. Since it was used along with the Lonzaines in this work, could it cause a misreading of the softening effect of the synthetic fatliquor?

MR. VIOLA: We have also done work on chrome leather without any glutaraldehyde, and secured the same effects. We like to use glutaraldehyde because of the color leveling and washability it confers on garment leathers.

MR. JOHN ARM (A. R. Clarke Company, Ltd.): Would you care to speculate on the chemical nature of the combination of the Lonzaines with the hide substance?

MR. VIOLA: The Lonzaines are quaternary ammonium compounds.

MR. ARM: Which groups in the hide substance are reactive?

MR. VIOLA: We did not check this.

DR. FILACHIONE (Eastern Regional Research Center): Since the chrome-tanned stock is cationic, we think that interaction results from an ionic attraction. Since the Lonzaines are amphoteric, there could be fixation between the cationic centers of the leather and the anionic centers of the agent. There could also be complex formation between the chrome centers and the derivatives, which are α-amino acid derivatives which can form metal complexes. However, this is speculative, since we have not investigated the reaction mechanism.

QUESTION: Did you notice any change or influence of these lubricants on the leather colors?

MR. VIOLA: The color stays essentially the same. We have used both acidic and reactive dyes.

QUESTION: What about basic dyes?

MR. VIOLA: We are just starting to consider basic dyes.

DR. E. HEIDEMANN (Institut für Makromolekulare Chemie, Darmstadt): Since the Lonzaines have a restricted solubility in water, you use an ethanol-water solvent. Since this would be difficult for tannery use, would you please comment on the solubility problem?

MR. VIOLA: Only the long chain Lonzaines required the ethanol-water solvent. The shorter chain Lonzaines are water soluble and would be the compounds of choice for tannery use.

DR. HEIDEMANN: In view of your results with the drycleaning detergent, could you use the detergent to promote the uptake and the distribution of the Lonzaines into the leather?

MR. VIOLA: We have not studied this possibility.

MR. DAVID R. SMALL (Saco Tanning Corp.): Have you investigated the compounds on other skins or hides?

MR. VIOLA: We have done a little work on splits. We have worked with goat, pig, cow, and calf with the Deriphats with the same results.

MR. I. LEO RIESE (Fermon Tanning Company): What are the prices of these materials in commercial grades?

MR. VIOLA: The Lonzaines are about 70 cents per pound for 30 to 35 percent active material.

MR. RIESE: What level would be used on the blue weight?

MR. VIOLA: Fifteen percent would yield a soft garment leather, *i.e.*, five percent active material.

MR. MILTON BAILEY (U. S. Navy, Natick): What is the substantivity of the Lonzaines to other fibers?

MR. VIOLA: We have not studied other fibers.

Mr. Milton Bailey: What about antistatic properties and flammability?

Mr. Viola: There may be a little static generated when the moisture content of the leather is below ten percent.

Mr. S. Panzer (Robson-Lang Leathers Ltd.): Who manufactures these products?

Mr. Viola: Lonza Inc., Fairlawn, New Jersey. Their Mr. Stan Elman, new products manager, is here. General Mills manufactures the Deriphats.

Mr. I. Leo Riese: There is a lot of interest in light-weight garment leathers. How does the specific gravity of the leathers using these materials compare with those with normal fatliquors?

Mr. Viola: We did not notice any difference from the commercial leather.

Dr. Heidemann: Normal fatliquoring requires long chain fats for lubrication. What about your materials?

Mr. Viola: We could not distinguish between the various Lonzaines in the final leather. However, the 18S long chain product, which would require the ethanol-water solvent, may not be practical in a tannery.

Mr. Riese: Does the garment leather color change after drycleaning?

Mr. Viola: When fast colors are used with the Lonzaines we have noticed no color change in drycleaning. Our work with the reactive dyes and the Deriphats showed that the colors do not change as a result of drycleaning.

Mrs. Tancous: We certainly appreciate the fine paper presented by Mr. Viola. I would like to present this certificate of appreciation to express the Association's gratitude.