

THE CHEMISTRY OF GLUTARALDEHYDE TANNING AND THE PROPERTIES OF  
GLUTARALDEHYDE TANNED LEATHER. A REVIEW AFTER TWENTY YEARS PRACTICE.

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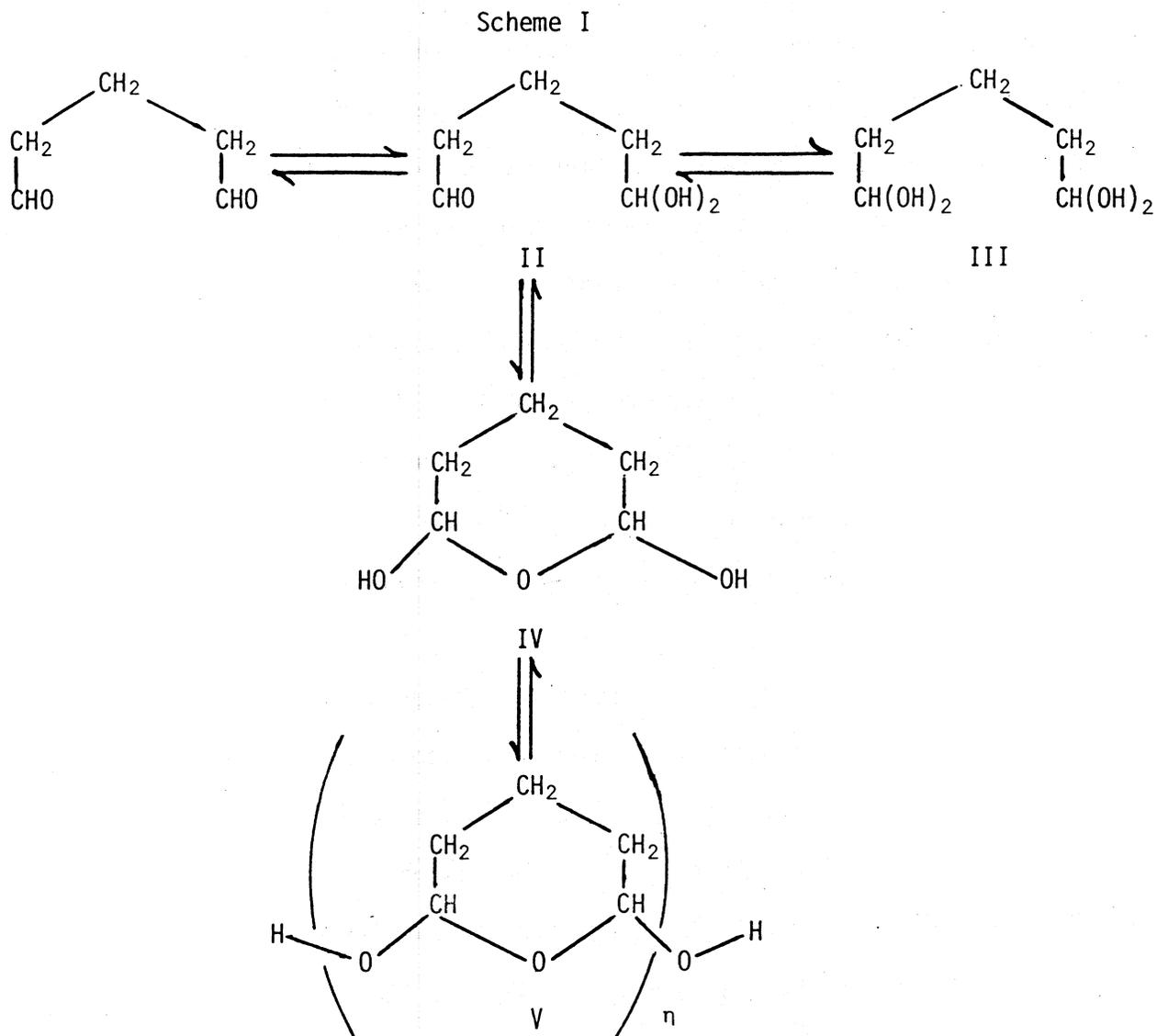
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In 1957, in two papers that appeared in the same issue of the *Journal of the American Leather Chemists Association*, Seligsberger and Sadlier (1) and Fein and Filachione (2) reported the initial results of studies which demonstrated the effectiveness of glutaraldehyde as a tanning agent. In a series of papers (3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13) that then followed from the Hides and Leather Laboratory of the Eastern Regional Research Center, USDA, the broad utility of this tanning agent was further demonstrated. Generally, glutaraldehyde is not used as the only tanning agent but rather in combination with other tanning agents or as a retanning agent. In recent years, about two million pounds of the commercial tanning agent are used annually in the United States and a like amount is exported. Information concerning its production and use in other countries is not available to us but its use is worldwide. In addition, various mixtures or chemical combinations of glutaraldehyde with other materials are recommended as pretannages, tannages, and/or retannages (14, 15, 16).

Despite this widespread use and interest, neither the chemical mechanism of the tanning reaction of glutaraldehyde and hide protein nor the nature of the products formed is known. The nature of the tanning reagent itself has been studied by a variety of groups, including those scientists interested in its use as a fixative for histochemical studies, others interested in its use in binding enzymes to solid supports, as well as leather chemists. Two schools of thought have developed regarding the actual tanning agent. One school proposes that a condensation polymer of glutaraldehyde containing

conjugated unsaturated aldehyde groups is the tanning reagent. This proposal is based on the ultraviolet absorption characteristics of the commercial tanning agent (17, 18). These polymers, formed by aldol condensations, are almost certainly present in many solutions of glutaraldehyde. They are responsible for and detectable by their ultraviolet absorption at 235 nm. However, the amounts present have been shown to be quite small (19, 20), about 7-8%, and various means have been used for their removal (21, 22, 23). The other school holds that glutaraldehyde itself is the tanning agent (19, 20, 22, 23, 24), and it has certainly been adequately demonstrated that purified solutions of glutaraldehyde are capable of tanning.

Much of this material was discussed in a paper by Heidemann and Bresler (25) five years ago and again three years ago by Keller, Heidemann, Rutkowski, and Milesan (26). The only additional information that can be presented is in the form of observations based on a review of these references. All agree now that aqueous solutions of glutaraldehyde, from which the condensation polymers have been removed, contain the compounds shown in Scheme I in varying amounts and in equilibrium with each other (19, 20, 22, 24). It was shown (19) that this equilibrium is temperature sensitive and that at higher temperatures more free aldehyde (I, II, or I and II) is present. Since free aldehyde must be present for an aldol condensation to take place and condensation products to form, the effects of temperature on the stability of glutaraldehyde solutions found by Gillette and Gull (23) are not surprising. Storage at lower temperatures (-20°C. and +4°C.) resulted in no or very little formation of the condensation polymer, as determined by absorption at 235 nm. However, storage at higher temperatures (+20°C. and +37°C.) resulted in a much greater formation of the polymer. It must be remembered, however, that the absorption of



conjugated, unsaturated aldehydes is as much as several hundred to a thousand times stronger than that of a saturated aldehyde. Therefore, a small amount of the former will exhibit a strong absorption maximum and overwhelm the absorption of the latter.

The aldol condensation reaction leading to the formation of unsaturated aldehydes and responsible for the formation of the polymeric impurities in

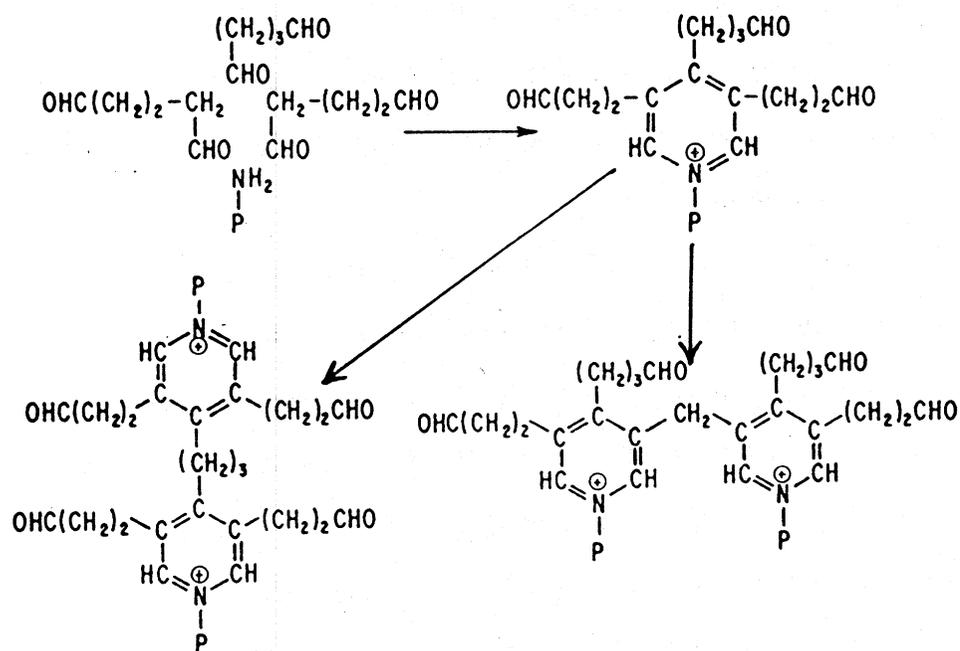
glutaraldehyde solutions is certainly a facile and rapid reaction and quite susceptible to general acid-base catalysis. The conditions found in most tanning reactions, especially at elevated temperatures, and the materials present, both acids and bases, are favorable for this type of reaction. Under these conditions, I do not believe that we can rule out the possibility that aldol condensation reactions and products derived from them are involved in the tanning reaction, especially when we also consider the complexity of the products formed. In fact, Richards and Knowles (17) and Monsan and coworkers (18) feel that only through such a mechanism can the stability of the glutaraldehyde tannage be explained and that a Michael Addition reaction is also involved. Heidemann and coworkers have also considered this possibility (25, 26).

Numerous studies of the nature of the products formed on reaction of glutaraldehyde with proteins have been conducted using a variety of model compounds as the source of the lysine, the amino acid involved to the greatest extent in the reaction. These model compounds have included 1-amino hexane (26), 6-amino hexanoic acid (27),  $N_{\alpha}$ -carbobenzoxy lysine (19, 26), hippuryl-lysine (19), polylysine (19) and  $N_{\alpha}$ -tosyllysine ethyl ester (25) in addition to others. In all of these studies, the product mixture exhibited the ultraviolet absorption at 265 nm characteristic also of glutaraldehyde-tanned hide collagen (28, 29). The studies conducted by Heidemann and coworkers (26) included use of a wide variety of separation and characterization techniques but only resulted in further demonstrating how complex the problem is. It was found in our laboratory (30) that the chromophore responsible for this absorption at 265 nm is reducible with sodium borohydride, a reagent also used by Heidemann and Bresler (25) to study its effect on the properties of the glutaraldehyde-tanned hide. We have used (30) the reagent with radio-

active tritium in place of the hydrogen to radioactively label the products. While we did successfully label the products, we could not successfully isolate and characterize any of them. This has also been the experience of others.

Perhaps the most significant of these studies is that of Hardy, Nicholls, and Rydon (27). On the basis of their studies, they have proposed the following (Scheme II) as the most likely, in their view, course of the reaction and products formed. (P is intended to represent the protein and the NH<sub>2</sub> the ε-amino groups of lysinyl residues.)

Scheme II



The properties of products isolated by us (19), using polylysine, N<sub>α</sub>-carboxy lysine, and hippuryllysine as model compounds, are such that the products could have structures similar to these. However, if these are the

products formed, it is not obvious why glutaraldehyde should be unique among the dialdehydes and why succinaldehyde or adipaldehyde were not equally effective (31). One less or one more methylene group should not have made a difference. In any case, the problem is a complex one and not amenable to an easy solution

The properties of glutaraldehyde-tanned and glutaraldehyde-chrome combination tanned leathers were reported in some of the earliest papers (3, 4, 5, 6) and the improvements resulting from the use of glutaraldehyde were adequately noted. These improvements include more level coloring of the leather, better mellowness, improved resistance to hot soap solution, resistance to perspiration, and resistance to alkalies, all of which have contributed to its use in leather for gloves, garments, work shoes, nurses' shoes, and ice skate shoes and shearlings for bedpads and paint rollers. This has been reviewed (7, 32) and is well known.

The adverse effects of glutaraldehyde tannage on the strength properties of the leather were not discussed in these early papers but were evident in some of the data, notably the stitch tear strength data (3). An extensive study of these adverse effects has been conducted by Heidemann and coworkers and reported in two publications (25, 33). While there are some inconsistencies between the results reported in these two studies, the general conclusion was that glutaraldehyde retanning does cause an increase in thickness and a decrease in tensile and stitch tear strength. These changes are, however, exactly the same as those obtained on washing the chrome-tanned stock with acetone and a direct correlation was found between the resulting percentage increase in thickness and percentage decrease in stitch tear strength (33). The same relationship has been found in our graft polymerization studies (34), although the only direct correlation found was

between the amount of polymer and the increase in thickness.

In any case, the adverse effects of glutaraldehyde tanning on the strength properties of the resulting leather are certainly not excessive and the improvements in other properties outweigh them.

Certainly, combination tanning with chrome and retanning following chrome are the major uses of glutaraldehyde (4, 6). However, it can be used quite effectively with vegetable tanning as a pretanning agent (8, 10). The penetration of the extract was very rapid and the properties (shrinkage temperature, water solubles, and perspiration resistance) were improved. Use as a retannage following vegetable tanning has also been studied (35, 36, 37). Essentially the same results, increased thickness and decreased strength, were obtained as noted above (25, 33) concerning the retanning of chrome-tanned leather.

Glutaraldehyde represents the latest in the development of major tanning agents for the tanning industry. It, like its predecessors, has many advantages and some disadvantages. These, taken together, limit it to use almost entirely as a retannage and for the manufacture of specific types of leathers.

It is interesting and probably misleading that a chemical as simple as a five carbon dialdehyde is as effective as it is. Research has made it clear that the simple five carbon compound, glutaraldehyde, is not itself the effective compound present after tannage. The complex chemistry of the glutaraldehyde tannage and the products formed belies the practicality of reliance on simplistic concepts in the search by leather scientists for additional tanning agents.

1. Seligsberger, L. and Sadlier, C. Jour. American Leather Chemists Assoc. 52, 2 (1957).
2. Fein, M. L. and Filachione, E. M. Jour. American Leather Chemists Assoc. 52, 17 (1957).
3. Filachione, E. M., Fein, M. L., Harris, E. H., Luvisi, F. P., Korn, A. H., Windus, W., and Naghski, J. Jour. American Leather Chemists Assoc. 54, 668 (1959).
4. Fein, M. L., Filachione, E. M., Naghski, J., and Harris, E. H. Jour. American Leather Chemists Assoc. 58, 202 (1963).
5. Windus, W. Jour. Soc. Leather Trades Chemists 47, 524 (1963).
6. Filachione, E. M., Fein, M. L., and Harris, E. H. Jour. American Leather Chemists Assoc. 59, 378 (1964).
7. Filachione, E. M., Fein, M. L., and Harris, E. H. The Leather Manufacturer, February 1964.
8. Luvisi, F. P. and Filachione, E. M. Jour. American Leather Chemists Assoc. 63, 584 (1968).
9. Happich, W. F., Happich, M. L., Windus, W., and Naghski, J. Jour. American Leather Chemists Assoc. 64, 227 (1969).
10. Hannigan, M. V., Windus, W., and Naghski, J. Jour. American Leather Chemists Assoc. 65, 451 (1970).
11. Happich, M. L., Palm, W. E., and Windus, W. Jour. American Leather Chemists Assoc. 66, 364 (1971).
12. Hopkins, W. J. and Bailey, D. G. Jour. American Leather Chemists Assoc. 67, 552 (1972).
13. Harris, E. H. and Filachione, E. M. Jour. American Leather Chemists Assoc. 70, 269 (1975).
14. Miller, F. F. German Patent 2,243,826 (1974).
15. Siegler, M. U.S. Patent 4,060,384 (1977).
16. Alford, P. M. Jour. American Leather Chemists Assoc. 73, 250 (1978).
17. Richards, F. M. and Knowles, J. R. Jour. Molecular Biology 37, 231 (1968).
18. Monsan, P., Puzo, G., and Mazarguil, H. Biochimie 57, 1281 (1975).

19. Korn, A. H., Fearheller, S. H., and Filachione, E. M. *Jour. Molecular Biology* 65, 525 (1972).
20. Blass, J., Verriest, C., Leau, A., and Weiss, M. *Jour. American Leather Chemists Assoc.* 71, 121 (1976).
21. Anderson, P. J. *Jour. Histochem. Cytochem.* 15, 652 (1967).
22. Hardy, P. M., Nicholls, A. C., and Rydon, H. N. *Chem. Commun.* 565 (1969).
23. Gillette, R. and Gull, K. *Histochimie* 30, 162 (1972).
24. Whipple, E. B. and Ruta, M. *Jour. Agricultural Chemistry* 39, 1666 (1974).
25. Heidemann, E. and Bresler, H. *Das Leder* 25, 229 (1974).
26. Keller, Ch., Heidemann, E., Rutkowski, J. R., and Milesan, M. *Das Leder* 27, 176 (1976).
27. Hardy, P. M., Nicholls, A. C., and Rydon, H. N. *Jour. Chem. Soc. Perkin* 1, 958 (1976).
28. Filachione, E. M., Korn, A. H., and Ard, J. S. *Jour. American Leather Chemists Assoc.* 62, 450 (1967).
29. Korn, A. H. and Filachione, E. M. *Jour. American Leather Chemists Assoc.* 62, 507 (1967).
30. Fearheller, S. H. Unpublished results.
31. Cater, C. W. *Jour. Society Leather Trades Chemists* 49, 455 (1965).
32. Naghski, J. *The Leather Manufacturer*, May 1967.
33. Keller, Ch., Heidemann, E., Rutkowski, J. R., and Milesan, M. *Das Leder* 27, 176 (1976).
34. Harris, E. H. and Fearheller, S. H. *Polymer Engineering and Science* 17, 287 (1977).
35. Restek, I. *Curo Pelli Mater. Conciante* 52, 19 (1976).
36. Restek, I. and Bravar, M. *Koza Obuca* 25, 6 (1976).
37. Restek, I. and Bravar, M. *Hem. Ind.* 32, 144 (1978).