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RECENT DEVELOPMENTS IN LEATHER AND THEIR RELATION TO NATIONAL DEFENSE

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History tells us that the wheel first came on the horizon of recorded civilization when it was invented by the Assyrians several hundred years B. C. It is amazing to know that the distance between the wheels of the ancient Assyrian chariots was almost exactly the same as that of our standard gauge. All through these centuries the distance between the wheels of wheeled vehicles has remained the same. Apparently this has been due largely to the fact that it was easier to follow in the ruts left by other vehicles than to attempt to change the gauge. Only with the development of hard surfaced roads in relatively recent times have we been able to get away from the standard gauge.

This is a parable of research, and not less so in its application to market research than to technical research. As a matter of fact, it has only been by the application of the principles of market research in quite recent times that the distribution of goods has gotten out of the ruts of the conventional concepts of past generations.

As one looks at the field of leather, its tanning and subsequent manufacture, one might say that on the one hand it is a fairly simple field for the market research analyst to study, since the total size of the market for chemicals in this industry can readily be ascertained. This is the case because of the very simple principle that the number of domestic hides available to tan will be proportional to the amount of meat prepared to serve on the American dining table, since the basic domestically produced material for leather is, a by-product of the packing industry, for which good basic statistical data are available. Similarly the number of imported hides can readily be ascertained from import statistics.

On the other hand, the leather industry might be regarded as the market research man's nightmare, because the application of any material to tanning of leather follows less the application of engineering principles or scientific reasoning than the craft of the artisan. When one seeks to find out why a particular material can or cannot be used in the production of leather, there is little in the way of firm data which can be found to indicate what affect it may have other than the ultimate judgment of the eye and hand of the skilled examiner of the finished leather that it appears to be all right. It is a field in which the scientific study of the physical properties of materials is still in a rudimentary state, and where research techniques for evaluating even relatively gross differences in physical characteristics resulting from the application of different materials are very limited, for those this presents a difficult problem. It is a problem to us as well, even though

of you in the chemical industry who are interested in this field of leather as a potential market for products you now make or are planning to make, ours is a quite different interest - that of the consumer of your products.

Thus, it may be said that the interest of the National Military Establishment in research and development of new chemical products for the leather industry is two-fold: first, our desire to improve the functional performance of military footwear and equipment made from leather, which in turn can be accomplished only by improving the physical properties of military leather; second, the necessity for obtaining relief from the stark fact of the almost complete dependence of this country upon imports of tanning materials, which could not be expected to be available through import in adequate quantity in time of war. The Leather Research Program of the Research and Development Branch of the Office of The Quartermaster General is directed along both of these lines.

There is no secret to the fact that the domestic supply of vegetable tanning materials is comprised almost wholly of the uncut stand of dead chestnut trees in the Southeastern Appalachian forests. These trees, which were killed by the blight some years ago, are the sole source of chestnut tannin, which in turn is the only important tanning material which is produced in this country. On an optimistic basis, what trees are left might supply a sixth of the industry's normal requirements for another ten years. Beyond that time there is no source in the products of forest and farm which can be counted upon at this time to supply any significant amount of the leather industry's needs of tannin.

It is true that the U. S. Department of Agriculture has for many years been studying alternative sources of tannin in the bark of other trees, and from annual plants like canaigre, a dock-like plant which can be grown in the arid regions of the Southwest. Up to this date, none of these products provide commercial sources for tannin for the leather industry as a whole. Small amounts of tannin from some of these sources are understood to be in use, but their limitations, either technical or economic, far overshadow such restricted use.

In this category are such sources as Western hemlock bark and redwood, from both of which tannin extracts might be produced for the leather industry. Production of a commercial tannin extract from the former has been considered to be uneconomic under the methods of lumbering currently in use in the Pacific Northwest; whereas the development of a satisfactory tannin extract from redwood has up to now been prevented by technical considerations.

Currently the Department of Agriculture, under urging from our office and the Munitions Board, is attempting to expedite the completion of technical research on the growth and extraction of tannin from canaigre roots. This source is one of the most promising of these alternative sources, since its roots contain as much as 40 percent tan. It is believed from both laboratory and limited plant tests that good tannage may be obtained with this extract, but full evaluation of it awaits successful separation of the tannin on a commercial basis from the start of the plant.

Another approach to providing a domestic source of tannin for the leather industry is believed to lie in the utilization of lignosulfonates and other by-products of the pulp and paper industries. The chemical structure of the lignosulfonates provides promise of tanning properties. Lignosulfates have seemed an obvious source for an inexpensive material for tanning leather, and in fact, certain derivatives of lignin are now used in tanning blends and as filling agents in heavy leathers. Such use is a far cry from replacement tannins, but the hope remains that by better understanding of the nature of the tanning process and the fundamentals of the action of tannin, some way may be found to convert such materials into active tanning agents. The Institute of Paper Chemistry three years ago under a research contract from the Quartermaster Corps initiated study in this field, and is currently continuing this study in conjunction with a number of the large firms in the paper and pulp industry who are deeply interested in development toward this end.

The necessity for finding a substitute for quebracho is accentuated by the fact that this material is also being used in large quantities as a mud conditioner in oil well drilling; hence, any supply which might be available in this country would have to be shared with the Petroleum

Industry. It is significant, however, that the properties of the material which make it desirable for use in drilling muds are quite different from those which enable it to tan leather. Hence it is reasonable to assume that materials which might not be satisfactory for tanning leather might serve adequately for oil well drilling. As a matter of fact, such is actually the case, and products from pulp and paper mill waste, which will not tan leather, already have replaced quebracho for oil well drilling through certain types of rock strata.

While research is being continued to find a new natural sources of tannin in products of forest and farm, two lines of development in the synthetic chemical industry are proceeding to lessen militaty dependence upon agricultural tannins.

The first is the development of true synthetic tanning materials. By this is meant replacement materials which actually substitute for natural vegetable tanning materials. One such material, Orotan, made by the Rohm & Haas Company, is now on the market and is being used commercially to a limited extent at the present time in the tanning of leather. Until recently the price differential between this material and natural tanning agents has been too great to permit wide scale use of it in leather manufacture. Recently with the substantial increase in the price of quebracho by the international cartel which controls its production, the differential has narrowed somewhat.

Evaluation of Orotan as to its utility in tanning military leather is currently underway. A full scale plant trial to produce all of the sole leather components for military footwear, using 100 percent Orotan is just now being completed. Approximately 16,000 pairs of shoes are being made, from which a trial lot will be tested to determine the suitability of this material for 100 percent replacement.

It is not surprising, accordingly, that there should be other tanning materials under development in industry. Several such materials are known to be in development. Announcement was made at the American Chemical Society meeting in September 1948 in Washington of a new process developed by Winheim and Doherty. This process is based upon a new principle of tanning by which the tannage is performed in two stages. The first involves reaction of the hide with a dialdehyde such as monomeric glyoxal. The first stage of tanning produces a piece of leather which is not too impressive in physical properties, but one which is said to be chemically reactive, and which accordingly permits reaction with resins, such as the ureas and/or phenol aldehydes. Polymerization is accomplished in situ with the polymer chemically bound to the dialdehyde used in the first stage of tanning. The rate and character of the polymer formed influences the character of the leather. An interesting thing about this approach to tannage is the possibility which it shows of producing leather with definite and controllable physical properties.

No public announcement has yet been made with respect to some of the other new tannages which are understood to be still in the development stage. However, this country has been the recipient of a great deal of information about developments in synthetic tanning materials made in Germany during the war. The technical investigators sent to Germany by the Office of The Quartermaster General brought back a great deal of information about the "tanigans" and related products developed by the I. G. Farbenindustrie. This information, together with other data obtained on the development of German replacement tanning materials has been included in three Leather Series Reports prepared by the Research and Development Branch, Office of The Quartermaster General.

Leather Series-Report No. 2 - "German Synthetic Tanning Agents"

Leather Series-Report No. 3 - "German Exchange Lipids for Leather"

Leather Series-Report No. 4 - "The Tanigan Extra Stuffing Materials".

These reports are available from the Tanners' Council, where they are regarded as of such importance that they have been reproduced for distribution to the Tanning Industry, and also from the U.S. Department of Commerce.

The success of the Germans in obtaining new synthetic tanning materials from the chemical industry, that were adequate to take them through the war, is certain to stimulate our own chemical industry which has a similar opportunity, not only in the event of a national emergency, but even in peacetime when we are wholly dependent upon imports of such materials.

The second way in which the chemical industry is lessening the demand for natural tanning materials is by the outright replacement of leather by synthetic materials in the components of soles, such as the outsole, insole, welt, midsole, and heel lifts, as well as in mechanical leathers.

The substitution of the composition sole for leather soles on combat footwear by the Army was a major replacement of this type. As a matter of fact, it would have been absolutely impossible to have supplied the Army with sufficient footwear using leather soles, since the composition sole was found to have several times the life of the leather sole.

The development during the war of Neolite and related compounds has opened up the possibility of rather large scale replacement of sole leather by these materials. This type of product is generally produced as a synthetic rubber type of compound with a low butadiene and a high styrene content. It has been found to provide a quite serviceable outsole, and one which actually wears longer than natural vegetable tanned leather. Replacement of sole leather by the Neolite type of compound is currently under test in the Army's shoes, low quarter, tan, which is the only major Army item of footwear which has not already shifted to a synthetic sole in place of leather. The principle question to be resolved is one of comfort, whether the synthetic rubber sole provides as comfortable a sole as leather.

What has been said above refers to vegetable tanning materials used principally in sole components, and for retanning of upper leather for heavy duty footwear. Most upper leather used in civilian shoes is chrome tanned, but Army upper leather, in addition to being chrome tanned, is then retanned with vegetable tanning material. This retannage makes for more comfortable shoes, and leather which dries out softer.

In the other major division of leather manufacture, chrome tannage, there is the same problem of potential shortage arising from dependence upon imports for our chemical chrome ores. Here chrome, as basic chrome sulfate, is used for the primary tannage of all Army shoe upper leather, and as the tannage for upper leather for the low quarter oxford, for gloves, and for the bulk of civilian shoe uppers.

As a matter of fact, leather can also be tanned with alum, zirconium and iron compounds in place of chrome. None of them give as good a tannage for Army shoe leather as chrome, although both alum and zirconium tannage have been used for other types of leathers. The technical literature is full of the history of attempts to tan leathers satisfactorily by using alum and iron. Neither tannage has achieved a permanent place in the tanning of Army leathers as the technical difficulties have not yet been overcome. Whether tanning methods using iron or alum can be improved or adapted in some way to deal with this situation is currently being made the subject of a research study under a contract of the Research and Development Branch with Lehigh University.

There is a further type of synthetic tannage which has recently been announced, which has been derived from the work of the Germans in their development of synthetic tannages. This is the "Immergan" or sulfonyl chloride tannage, otherwise referred to as an oil tan. Its most obvious application is to chamois leather, white leather and garment leather generally. It also shows promise of being usable for some other leathers. This development was first explored in this country at Ohio

State University, working jointly with the Tanners' Council Laboratory at the University of Cincinnati, under research contracts of the Research and Development Branch, where leather tanned by this process was produced on a laboratory scale. Considerable progress has since been made in advancing the application of this process by the duPont organization who are actually carrying on research on this type of tannage.

The "Immergan" type of development brings us to another development of far-reaching importance in the production of leather, which may have even more immediate application to military leather. This is the production of synthetic stuffing and fat-liquoring materials for leather. During the war shortage of fats led to the production of a whole range of synthetic materials in Germany, even edible fats, from the hydro-carbons derived from the Fischer-Tropsch Process.

Oils, fats and greases are needed in the finishing of leather to impart particular properties to the leather and to lubricate the material internally. Tensile strength, tear resistance, prevention of cracking and similar properties are influenced in very considerable part by the presence of these materials, which seem to surround the fibers of the leather and permit the fiber bundles to move over each other when the leather is flexed. The most satisfactory of the German synthetic fats were the "Derminols" which they used in replacement of tallow, neats-foot oil, and train-oil.

One of the most interesting of these products, Derminol Grease 2, is a mixture of a chlorinated fraction from the Fischer-Tropsch Process and a chlorinated synthetic hard wax. It had about the consistency and viscosity of a conventional mixture for stuffing of heavy upper leather, and was used rather extensively by the Germans on military leather.

It is obvious that it is unnecessary to go back to the same sources of materials as were used by the Germans in their extreme emergency, and that there should be many analogues of their raw materials which should be available in this country from the petroleum industry that could provide a starting point for a synthesis based upon domestically available materials. As a matter of fact, a great many materials are available for the purpose, including straight chain hydrocarbons of 10 to 20 carbon atoms, which, when chlorinated appear to be relatively stable under ordinary storage conditions. It is at least possible that some of these materials might be produced commercially at even lower prices than the natural stuffing materials which they might replace.

Research on the production of synthetic stuffing and fat-liquoring materials for leather is currently continuing under Research and Development contracts with Ohio State University and the University of Cincinnati, in the Tanners' Council Laboratory. Pilot plant scale production of leather, using several very promising materials, is currently under way.

From the above discussion it would be apparent that developments in leather technology, and research and production in the chemical industry are proceeding on a rather broad front. It may be that this decade may later be found to be one of the most revolutionary for this industry, or at least one in which major new lines of technological progress have been opened up.

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To return to the first of the two aspects of leather research which I mentioned at the opening of this discussion, a word or two should be said regarding the improvement of the functional performance of leather military footwear and equipment.

We visualize this requirement as falling into four general areas: Improvement of the water resistance of leather, improvement of its wear resistance, improvement of its stability as a chemical product, and finally the improvement of the comfort factor, or at least its retention at the level of good leather quality while simultaneously improving leather in other respects.

Before discussing the other aspects, it would be well to comment briefly on this matter of foot comfort. Without going into the basic physiology involved, it may be mentioned that foot comfort partakes of two or three different aspects. We have to begin with the emplacement of a fleshy structure within a case of fixed dimension. The flesh of the foot must mold itself according to this structure. If proper fit is not obtained, discomfort will result. This is basically a matter of shoe lasts, shoe sizing and fit. A second aspect pertains to the relationship of the anatomy of the foot to the body in motion: the interaction of the bony and muscular structures when emplaced within a shoe with the body either at rest bearing its weight or in motion. This is a problem in part of the conformity of the foot to the bottom of the shoe, that is, the surface of the insole and the sole structure.

The quality of foot comfort here may be interpreted in many ways, some of them related to the foot and others related to other parts of the body. In part this is a problem of the flexibility or rigidity of the materials in the shoe, in part it is a problem of shoe design and construction, and in part is a matter of the condition and structure of the foot itself.

A third aspect, and the most important from the standpoint of the leather, is the relation of the shoe to the foot as a body structure, from which moisture is given off both as insensible perspiration, normal perspiration from the foot area, and perspiration resulting from emotional disturbance. Just how much moisture one should expect to be given off as perspiration has not been adequately determined. However it is a matter of common experience that under certain temperature and humidity conditions, unless the foot covering is moisture vapor permeable, definite discomfort will result.

As a matter of fact, this problem of getting rid of body moisture resulting from perspiration is one of the most critical problems of military research in the field of environmental physiology. It is also a critical problem of materials engineering in the field of clothing and footwear to obtain materials and clothing constructions which will keep out exterior moisture from rain, fog, mud and underbrush, while at the same time permit free passage of moisture outward from the body. The term "one-way permeable" has been used to describe the kind of material which is sought in order to retain a modicum of comfort. Leather in its ordinary tannage is inadequate as a material for military items if we consider that this required property is of fundamental importance. There is no way known at present, all the oil compounds for filling up leather to the contrary notwithstanding, for so treating leather as to retain its vapor permeability, while at the same time to make it resistant to passage of water from the exterior under dynamic conditions.

For some time our office has been deeply concerned over the inability of leather technology to deal with this problem. It has seemed to us that the conventional concept of producing leather by the use of oils, fats and tallows is not likely to be productive of the kind of solution which seems to be needed. These materials, which are referred to as stuffing materials, or in lighter leathers as fat-liquoring materials, perform a highly important function of lubricating the leather. However, their retention in the leather is apparently solely one of surface adhesion. Because of this, it is possible to remove them in use by any one of many ways.

Furthermore, the more oils and fats which are put into leather, the more is the water vapor permeability reduced, to a considerable degree in a direct proportion. In other words, attempts to make leather water resistant by the use of such oils and waxes simply cuts down the water vapor permeability as more of these materials are put into the leather.

Accordingly, our office several years ago initiated a study of the impregnation of leather with resins of small particle size which could then be polymerized in situ in the leather to the desired extent. By selection of the resins or similar materials it was considered feasible to lubricate the leather, at the same time making it impossible for the resins to be removed by any subsequent mechanical action. Other compounds such as acrylates and synthetic rubbers have also been used for this purpose. It was further desired that such impregnation should be carried out by processes which would be normal to the commercial tanning of leather so as to avoid processes which would require extensive readjustment of industry procedures.

The opportunities for modifying physical properties of leather which are suggested by this approach will be obvious. It should be possible to modify not only the water resistant characteristics, but also its wear resistance as well as its other mechanical properties.

In addition to the application of such resins and other synthetic materials to leather for gloves and uppers of shoes, the National Bureau of Standards under a joint project with our office has been exploring the impregnation of sole leather with resins, such as acrylates and rubbers. The implication of this, of course, would be that a treated leather sole would be vastly more resistant to wear, while at the same time retaining a great many or most of denied properties of the leather itself, depending upon the extent to which the impregnation is carried. Since sole leather now is loaded with at least a quarter of its final weight with any one of a number of materials, many of them water soluble, which simply fill it out and increase its firmness, it is obvious that the use of some of these materials having greater performance and having high resistance to abrasion, should be a very real contribution to the production of an improved product by the industry.

As in all such functional treatments and finishes of natural materials, there is a fine point of balance which must be achieved in order to obtain a desirable product. Here the balance must lie between the desirable natural properties of leather which must be retained, while at the same time obtaining the advantages to be offered by the particular compound used in the treatment. Nothing would be gained for example from any of these treatments if the resulting material had none of the desirable comfort and insulating properties of the original leather. The achievement of such a balance will require a careful balancing of both of the technologies concerned.

This brings us to the last of these functional properties of leather which I have just mentioned, namely, the stability of leather. Leather has one property which involves some risk to the military when we consider world wide operations. Under conditions of high temperature and humidity in storage, probably even around such temperatures as 120°F with relatively high humidity, it will tend to hydrolyze. Since it is not always possible to store any military item under ideal conditions, study is needed to insure that what we buy will be serviceable when we need to use it. For one thing, we are quite sure that there are levels of pH in the finished product which should be avoided, even though all leather is finished on the acid side. The introduction of any new compounds to provide a functional finish or quality must be related to this basic important characteristic of stability of the finished product.

In the final analysis, the Quartermaster Corps has no other reason for being, so far as this field is concerned, than to provide personal protection to the soldier. That is our first and foremost responsibility. While research in weapons is directed primarily toward increasing their effectiveness in destroying the enemy, or in other words, in learning how to killor disable more effectively, the Quartermaster Corps, like the Medical Department, has a mission to protect and save life. Where the Medical Corps seeks to restore injured or wounded men to health, or to prevent the inroads of disease, we seek to preserve the health of the soldier and to increase his efficiency through the improvement of his food, clothing, equipment and shelter in the field. It is our job to keep him healthy by giving him the right food and clothing which will protect against exposure in whatever environment he may be. Over and above that, it is our job to give him that extra ounce of stamina and endurance which will spell superiority in the struggle against both his environment and the enemy.

In our work and in that of those of you in industry who are working along with us in this same field, we need the highest level of creative imagination to advance technology concerned with production of items not only for military use, but for the public as well. The American public is aspiring to set higher standards of living and to live up to them. Is it expecting too much for us in the military who are striving to protect the boys from your homes who may some day have to fight for us, to hope for a higher level of performance for everything we give them than we are content with in civil life, and more efficient items than any potential opponent might have?