UNIVERSITY OF CINCINNATI

27 May 1949

I hereby recommend that the thesis prepared under my supervision by Wm R Cox

entitled A Study of Some of the Factors Concerned with the Phenomenon of Adhesion to Glass Plates

be accepted as fulfilling this part of the requirements for the degree of Doctor of Philosophy

Approved by:

Fred O'Flaherty

Form 668—G.S. and T.C.—500—5-45

A STUDY OF THE PHENOMENON

OF THE ADHESION OF WET LEATHER

TO GLASS PLATES

A THESIS

PRESENTED TO THE FACULTY

OF THE

GRADUATE SCHOOL OF ARTS AND SCIENCES

THE UNIVERSITY OF CINCINNATI

IN PARTIAL FULFILLMENT

OF THE REQUIREMENTS FOR THE DEGREE

DOCTOR OF PHILOSOPHY

1949

By

WILLIAM R. COX

B.S., Newark College of Engineering, 1941

M.S., Stevens Institute of Technology, 1947

ABSTRACT

An experimental method for measuring the adhesion of leathers to glass plates has been developed. By means of the method, variations in the adhesive character of leathers are demonstrated.

The effect of starch concentration, moisture content, flexibility and time of storage of leather samples was studied. Starch paste viscosity has only a secondary effect. An overall precision index of 15 per cent was obtained.

Certain of the constituents of the epidermal area of some leathers were determined, and the results were correlated with the adhesive character of the leathers. A positive correlation between the amount of fatty material present in the epidermal area and the adhesion is demonstrated. The correlation is not significantly affected by the type of dyestuff used nor the amount of chrome oxide determined. Certain anomalies in the correlation are discussed and a possible explanation suggested.

ACKNOWLEDGEMENTS

Grateful acknowledgement is extended to the Tanners' Council of America, who provided the funds which made this work possible. Sincere thanks are due to Dr. Fred O'Flaherty, Director of the Tanners' Council Laboratory, for his guidance, friendly advice, and constructive criticism.

A constant inspiration was the unflagging interest, leadership and genuine helpfulness of Dr. Robert M. Lollar and of Professor William T. Roddy under whose supervision the work was performed.

Acknowledgement is made of the splendid cooperation of the Fred Rueping Leather Company and the Ohio Leather Company, who supplied the many special leather samples required.

Thanks are due to Mr. Ben A. Grota for valuable technical assistance.

TABLE OF CONTENTS

TABLE OF CONTENTS (continued)

INTRODUCTION

The conversion of skins and hides into leather requires several major classes of operations, including: preparation of the skins or hides to receive the tanning material, tannage, lubrication, finishing, and drying. Although much research has been reported on the early stages of this process, the latter stages have received very little study. This is particularly true of the so-called paste drying process which has become the dominant drying method for certain types of leather. This thesis will present information which will permit a beginning to be made in the understanding of this complex process.

History of Pasting and Development of the Problem

In the pasting method the wet hides or skins are affixed smoothly and firmly to a glass or other pasting plate by means of a temporary adhesive. The leathers are then dried in a current of air at controlled temperature and relative humidity while in contact with the plate. With most leathers the grain surface of the leather is in contact with the adhesive on the plate. Increased area and a surface smoothness difficult to obtain by other means are claimed for the process. After the hides or skins are dried, they are carefully peeled off the supporting plates. Any residual adhesive is removed from the surface of the leather by means of a mild washing process, care being used to avoid completely rewetting the leather.

Since the inception of the pasting process in 1911 by Smith (1) one of the major problems has been the selection of conditions which insure the proper adhesion of the leather while wet and yet allow its easy removal when dry. During the course of the industrial development of the process, many plate surfaces, adhesive formulations and variations in the properties of the leathers were made. A review of the history of the pasting process is contained in a paper by Cox (2).

One of the most perplexing problems has been the causes of sticking of the dried leather to the pasting plates. At times the leather could be removed easily from the plates with no damage to the leather, while at other times it has been necessary to soak the leather off the plates in order to avoid severe damage to the grain surface. The nature of the problem has remained poorly understood. It has been suggested that the heterogeneous nature of the hides and skins themselves, any of the varied tanning operations, the adhesive formulations, or the drying conditions could well have considerable effect on the final adhesion of the leather. The review by Cox (2) revealed no previous systematic studies of the problem.

EXPERIMENTAL

The Experimental Approach

Figure 1 shows a diagram of the bond between the leather surface and the glass pasting plate. When the leather is removed from the plate, rupture of the bond may occur at the interface between A and B, or at the interface between B and C. Rupture may also occur within the film B or within the leather C.

If failure of the bond occurs selectively at the interface between B and C; i.e., at the interface between the adhesive film and the leather surface, then, perhaps, some insight into the adhesive character of the leather surface may be obtained.

Preliminary experiments have shown that, when the glass plates are carefully cleaned and dried before use, and when adhesive pastes prepared from cooked raw starches are used, failure will take place almost entirely at the leather surface-adhesive film interface. The leather surface is essentially free of residual adhesive while the almost intact adhesive film remains on the surface of the glass plate. The surface of leathers which had been paste-dried in the laboratory were examined by means of a low-power binocular microscope and were found to be very nearly free of adhesive.

In order to study the effect of the penetration of the adhesive into the hair follicles of the leather, small

FIGURE I

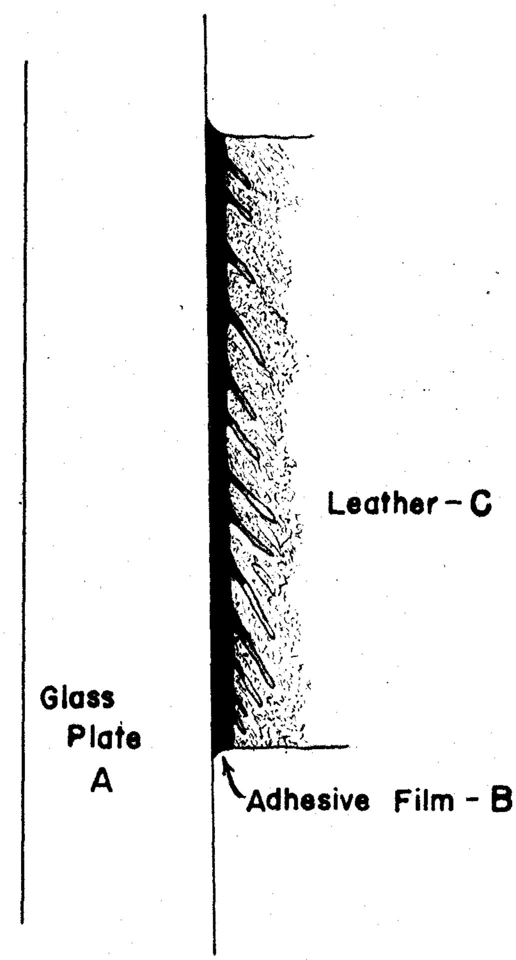

DIAGRAM OF ADHESIVE BOND BETWEEN LEATHER SURFACE AND GLASS PLATE samples of leather were pasted to cleaned micro slides. After drying, the leathers were removed from the slides and the course of the removal of the leather was watched through the base of the slide by means of a binocular microscope. In every case it was found that, if the leather was peeled off the slide slowly, rupture occurred first at and around the hair follicle. That is, the line of rupture crept ahead to include a complete hair follicle before the "lands"* between the hair follicles were removed from the slide. This shows that the adhesive bond at the hair follicles is much weaker than the bond between the "lands" and the glass slides. The adhesive effect gained by reason of the keying of the adhesive into the hair follicles is small.

In order further to study this keying, cross-sections were prepared from laboratory paste dried samples. These cross-sections were stained with iodine to show the presence of residual starch. The drawing (Figure 2) shows that the grain surface areas of the leather between the hair follicles are essentially free of adhesive. A film of starch is found in the immediate vicinity of the hair

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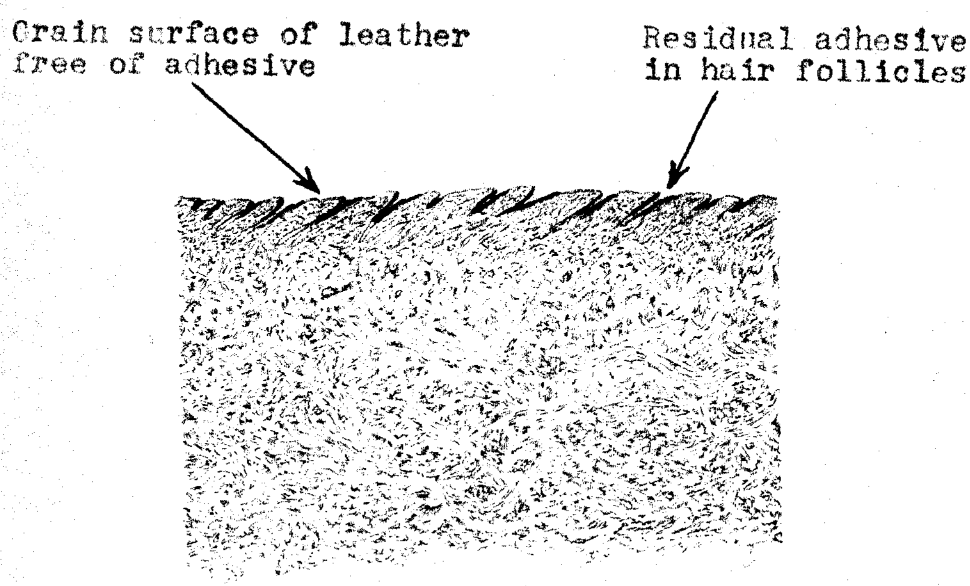
*"Lands" are the areas of the grain surface between the hair follicles where contact between the leather and plate occurs.

FIGURE 2



DRAWING OF CROSS SECTION OF

PASTED LEATHER

follicles and within the follicle to about one-third its depth. Rupture occurs within the film in this area. Either contact is poor and the film breaks away from the glass plate, or rupture may occur entirely within the adhesive film. It is seen, therefore, that the force required to peel the leather from the glass plate will be an average of the greater force required to remove the leather in the "lands" and the much weaker force required to remove the leather in the hair follicle area.

Development of Method for Measuring the Adhesive Character of Leather

In order to study quantitatively the bond between the leather surface and the adhesive, a laboratory technique was developed to affix leather samples to glass plates by means of a standardized adhesive, to dry the leathers under controlled conditions, and to measure the force required to peel the leather from the plate. The experimental procedure leading to the development of this technique is divided into the following parts:

(a) Preparation of standard adhesives.

(b) Procedure for affixing the leather to the plate.

(c) Measurement of the load required to peel the leather from the plate.

A. Preparation of Standard Adhesives

As previously pointed out, pastes prepared by cooking raw starches yield a bond which generally ruptures at the interface between the leather surface and the adhesive film. Further preliminary studies also demonstrated that adhesives prepared from such materials as methyl cellulose and some natural gums did not yield the required selective bond failure. Therefore, it was decided that all of the experimental work would be carried out with adhesives prepared from raw or unconverted starches.

Starches are prepared commercially from a variety of sources such as corn, tapioca, wheat, white potato, sweet potato, arrow root, sago, rice, and the newer hybrid, waxy corn. When starches are heated in water the granules swell, giving a rapid rise in viscosity of the paste. The viscosity of the resultant sol is due to the swollen granules or sacs and to the highly solvated colloidal micelles. The most important factor is the swelling of the granules. If the granules are broken the paste is greatly lowered in viscosity.

The temperature at which the starch granules swell is called the gelatinization temperature of the starch. The exact gelatinization temperature is a characteristic for a particular type of starch and depends to some extent upon the method used for its determination. Many studies of the swelling phenomena have been made (3). However, for the work at hand it was only necessary to demonstrate that starch pastes could be reproducibly prepared from batch to batch. The most generally accepted criterion for characterizing starch pastes is that of viscosity (4). However, starch pastes do not show normal Newtonian viscosity, that is, the apparent viscosity is a function of the method used for its determination. Starch pastes are also highly thixotropic, the pastes increasing in viscosity on standing and decreasing in viscosity when stirred (5).

Within the starch industry two types of viscosity determinations are normally used: (1) the "hot paste" viscosity, and (2) the "cold paste" body. The hot paste viscosity may be determined by means of the Scott test. In this test a known quantity of starch and water are heated in a boiling water bath with continuous stirring for a definite period of time (15 minutes). At the end of this time a definite volume of the paste is allowed to flow through a standardized orifice. For reproducible results, manipulative detail must be adhered to exactly. Determinations of the cold paste body are made by means of a wide variety of methods. For dilute solutions Ostwald type viscosimeters have been used. Other instruments include the Stormer viscosimeter, the MacMichael viscosimeter, the Brabender Amylograph (6), and the new Corn Industries Research Foundation viscosimeter (7). Bechtel (8) claims a reproducibility of ± 2 per cent for duplicate pastes made by different operators with the Corn Industries unit. All investigators agree that close control of the cooking conditions is required for reproducible results.

A laboratory procedure for preparing starch pastes was developed. Pastes were prepared by suspending a 500 ml. tall form beaker containing the starch slurry in a constant temperature bath adjusted to 95°C. Constant agitation at a uniform speed of 150 r.p.m. was applied throughout the cooking period by means of a rubber bladed paddle which scraped the sides of the beaker.

The water lost by evaporation from the starch paste during the cooking period was shown to be in the neighborhood of 5 - 10 ml. (see Table 1). An initial volume of 255 ml., when the pastes are cooked for 15 minutes and 260 ml. for a cooking time of 30 minutes, insured a final volume of 250 ml. of paste with a maximum variation of 2 per cent.

Starch concentrations are based on the dry weight of starch corrected for moisture and are calculated on a weight-volume basis. All samples were taken from the same batch of starch which was thoroughly mixed before use and kept in a sealed bottle. Moisture was determined by drying samples for 18 hours at 100°C. in vacuum. The weighing bottles were cooled in a desiccator over magnesium perchlorate. Sair and Fetzer (9) have shown that ordinary desiccants are ineffective. The starch samples were

TABLE 1

DETERMINATION OF EVAPORATION LOSSES
DURING COOKING OF STARCH PASTES

Cooking Time Min.	Final Temp. Water °C.	Temp. Bath °C.	Grams Loss
15	90	100	5.3
30	94	100	9.0
15	63	71	4.5

weighed to ± 0.02 gram. Distilled water was used throughout in the preparation of the pastes and was measured to ± 1 ml. The cooking time was determined from the time the starch slurry reached a temperature of 50°C. This was felt to give the most reproducible cooking time.

A MacMichael viscosimeter was used to determine the apparent viscosity of the pastes. In order to calibrate the MacMichael viscosimeter in absolute viscosity units (centipoises), an Ostwald, Fenske-Cannon viscosimeter, commonly called a Fenske-Cannon viscosimeter, was calibrated by means of a series of glycerol solutions using the method of Sheely (10). The specific gravity of the glycerol solutions was determined by the method of Bosart and Snoddy (11). The calibrated Fenske-Cannon viscosimeter was then used to determine the viscosity of a series of corn syrup solutions covering the range of the MacMichael viscosimeter.

Viscosities of the starch pastes were determined at 25.0°C. after an aging period of 18 to 24 hours. In all cases the value taken as the apparent viscosity was that obtained after a period of 5 minutes continuous running in a MacMichael viscosimeter. This was felt to be the most easily reproducible value, as the dial reading changes rather rapidly during the early minutes of run, while small changes are encountered after 5 minutes, as shown in Table 2.

TABLE 2

VARIATION IN APPARENT STARCH PASTE VISCOSITY

WITH TIME OF RUNNING IN MAC MICHAEL VISCOSIMETER

	Viscosity Centipoises					
Starch Paste	1 Min.	2 Min.	3 Min.	4 Min.	5 Min.	10 Min.
1% Potato	83	80	79	79	78	78
3% Potato	1710	1680	1650	1630	1620	1580
5% Potato	1970	1830	1770	1720	1700	1640

TABLE 3

VISCOSITY OF STARCH PASTES AS A

FUNCTION OF STARCH CONCENTRATION

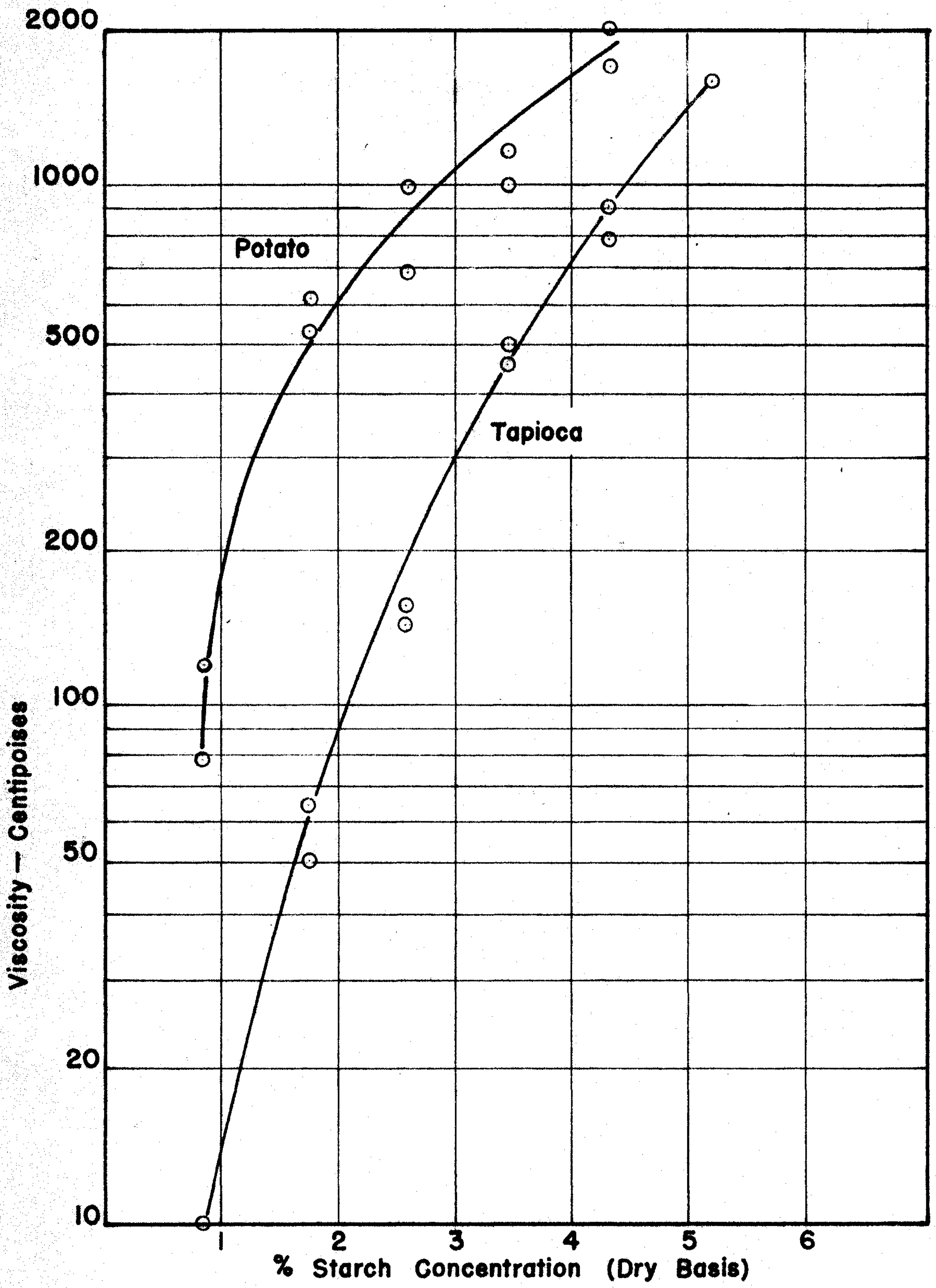
Potato Starch

Starch Conc. % Wet Basis	Dry Basis	Viscosity Centipoises
	Run 1	
1	.87	120
2	1.74	605
3	2.61	890
4	3.48	1350
5	4.34	2060
	Run 2	
1	.87	78
2	1.74	530
3	2.61	690
4	3.48	1000
5	4.34	1700

Tapioca Starch

Starch Conc. % Wet Basis	Dry Basis	Viscosity Centipoises
	Run 1	
2	1.73	50
3	2.59	145
4	3.45	500
5	4.32	790
6	5.18	1360
	Run 2	
1	.86	10
2	1.73	64
3	2.59	156
4	3.45	460
5	4.32	920

FIGURE 3



STARCH CONCENTRATION vs VISCOSITY

Potato and tapioca starch pastes of from 1 to 6 per cent concentration were prepared and their viscosity determined. Table 3 and Figure 3 are representative results.

B. Development of Technique for Paste Drying Experiments

The final paste-drying technique consists of the following critical steps:

(a) Standardization of the moisture content and flexibility of the leather.

(b) Coating of the leather with a film of standard adhesive.

(c) Mounting of the leather sample on the pasting plate.

(d) Drying the samples under standard conditions.

(e) Determination of the force in grams required to peel the leather from the plate under "constant rate of extension" conditions.

Before satisfactory results could be obtained it was necessary to develop an "integrated whole" process. Necessarily the development of the various steps was carried along together. However, the many factors which had to be considered are discussed separately for clarity.

I. Preparation of Leather Samples

After having demonstrated that starch adhesives of fairly reproducible viscosity were available, it was then possible to proceed with the development of a technique for making paste drying experiments. It was first necessary to select a type of leather and an area of skin for experimental work. Chrome tanned calf skin shoulders were selected for the work. This choice was made for the following reasons:

(a) The leather was readily obtainable from one of the large tanneries.

(b) The structure of the shoulders is fairly uniform over the area.

(c) The structure of the epidermal area of the shoulder in some ways represents an average of the epidermal area of the entire skin.

All leather samples were prepared by a tanner of calfskin leathers. The wet leathers were shipped to the laboratory in a condition ready to paste dry. By using only the center portions of the shoulders, samples are comparable structurally from lot to lot and possible variations may be minimized.

Upon receipt of the leathers at the laboratory, they were cut into 4"x6" pieces as shown by the diagram. Six 1"x2½" paste drying samples were then cut from each of the 4"x6" rectangles. The 1"x2½" samples were then made up into 16 samples each for paste drying experiments. In grouping the samples precautions were taken to mask skinwise and areawise variations. After wrapping in aluminum foil, all samples were stored in a "deep freeze" cabinet.

II. Choice of Plate Size and Preparation of Plate Surface

For ease in handling, 12" diameter circular glass plates were selected. These plates were obtained with a ½" diameter hole in the approximate center of the plate. The plates were cleaned by scrubbing with a commercial detergent (Orvus) and a mild abrasive. After thorough rinsing with tap and distilled water the plate surface has essentially a zero contact angle against water. Finally the plates were flooded with about 50 ml. of c.p. acetone to dry the surface quickly.

III. Drying the Samples

Drying of the samples was effected by placing the glass plates, bearing the attached samples, in a small electric oven. The oven was provided with automatic temperature control while humidity was controlled manually. During the drying cycle the glass plates were placed on a mandrel and rotated at a speed of approximately 150 r.p.m. Except where noted, all samples were dried at a dry bulb temperature of 62°C. and a wet bulb temperature of 50°C. These drying conditions were selected because they approximated mild commercial drying conditions. The time required to dry the samples was from 2 to 2½ hours depending on their thickness.

IV. The Determination of Adherence

After the samples were dried in the oven they were allowed to remain on a laboratory bench overnight. The determination of adherence was made by means of a "strip peel" test similar to the ASTM strip peel test for Rubber No. D903-46T (12).

A model X-5 Scott tester was obtained and modified for the purpose. A holder was constructed to mount the 12" circular glass plates on the drawbar.

By rotating the glass plate the leather samples were brought individually under the testing device. Two scales are provided on the instrument, one from 0 to 1000 grams; the other from 0 to 5000 grams. A pulling speed of 12" per minute was used in all the work.

Specimens for testing must be mounted radially on the glass plates. This is necessary to insure that the load will be directed across the 1" dimension of the sample.

In making the actual measurement the outer edge of the leather sample is lifted from the glass plate and clamped to the cable from the load measuring pendulum. The instrument is started, and the best average load in grams required to remove the sample is recorded.

V. Procedure for Standardizing the Leather Condition

Preliminary paste-drying studies tended to show that the results obtained were considerably affected by the condition of the leather at the time of paste drying. Variations in both the moisture content and the flexibility of the leather caused wide variations in the measured adhesion.

Through repeated trials a method was evolved which seemed to standardize both the moisture content and flexibility of the leather in a satisfactory manner. This procedure follows:

1. Remove samples from freezer and allow to that overnight in a refrigerator.

2. Flex the samples by doubling the leather grain inward and rolling the fold to the edge of the piece with the thumb and index finger, using firm pressure. Repeat twice from each end.

3. Place the flexed samples in a beaker of distilled water and allow to remain in the water for a minimum of one hour.

4. Remove sample from the water touching the grain surface of the leather at the ends of the sample only.

5. Place the sample grain side upward on the surface of a double thickness of Whatman No. 2 filter paper.

6. Double the filter paper over on top of the grain surface of the leather and press moderately with the fingers until the paper in contact with the grain of the leather is uniformly wet.

7. Remove the sample and flex again as in step 2.

8. Blot the sample again as in step 7 using a single sheet of filter paper.

9. Coat the sample as uniformly as possible with a thin film of adhesive. A ½" pure bristle brush is used for this purpose. Only a small amount of adhesive is taken up in the brush at one time.

10. Place the sample grain surface down in position on the plate. Press lightly into place with the fingers.

11. Cover the sample with a single sheet of filter paper and press into place with the flat handle of a spatula.

12. Remove the filter paper and check the sample to make sure that it has been uniformly applied to the plate.

In order to obtain an indication of the critical steps in the procedure, the following series of experiments were performed. Three per cent potato starch pastes were used in all of the experiments.

Test A-1 -- The samples were permitted to remain on the laboratory table for 48 hours prior to use, and were flexed before mounting.

Test A-2 -- The samples were permitted to remain on the laboratory table for 48 hours prior to use, and were not flexed prior to mounting.

Test B -- The samples were conditioned and mounted by means of the standard procedure previously outlined.

Test C -- The samples were permitted to remain in distilled water for about four hours, then blotted, flexed, and placed in a desiccator for 18 hours. The samples were mounted the following day without additional flexing.

Test D -- The samples were allowed to remain in distilled water overnight. The following day they were mounted by means of the standard procedure used in test B.

Test E -- The samples were allowed to remain in distilled water for 24 hours, then blotted, flexed, and placed in a desiccator over water for an additional 24 hours prior to mounting.

Test F -- The samples were allowed to remain in distilled water for 72 hours, before mounting by means of the standard procedure used in test B.

The data obtained are tabulated in Table 4, and the difference in the adhesion obtained from each experiment, compared to that of experiment B are shown. In order to ascertain whether the differences shown were the result of random fluctuations the (t) and (F) tests of Snedecor (13) were employed. In those cases where the data show significant differences, it is so marked in the table.

The results of these experiments show the following:

(a) Samples would be conditioned in water for from 1 to 24 hours but not longer.

(b) Samples should be flexed immediately before use.

(c) Storage in water for longer periods tends to increase the measured adhesion.

(d) Lack of flexing or conditioning in water prior to use tends to lower the measured adhesion.

VI. Effect of Starch Concentration on Adhesion

Studies were made of the effect of starch concentration on the apparent adhesion of two types of leather; one of high adhesion and one of low adhesion. These data were obtained for the dual purpose of obtaining an estimate of the precision of the paste drying method, and of the importance of the viscosity of starch pastes on the apparent adhesion.

TABLE 4

VARIATION OF APPARENT ADHESION

WITH METHOD OF CONDITIONING LEATHER SAMPLES

Test	No. of Samples	Mean Adhesion Grams	Standard Deviation Grams	Difference in Adhesion Compared To Test B	
A	8	638	64	- 112	Sig. at 1% level
A1	4	200	141	- 550	Sig. at 1% level
B	12	750	77		
C	12	681	57	- 69	Sig. at 1% level
D	12	804	91.5	+ 54	Not sig.
E	12	767	51	+ 17	Not sig.
F	12	904	140	+ 154	Sig. at 1% level

Two groups of leathers were obtained and samples prepared. Paste-drying experiments were then performed using these samples. Starch concentration was varied from 1 to 6 per cent. Pastes were prepared from both tapioca starch and potato starch. The tapioca starch series was used in addition to the potato starch series because tapioca starch pastes have a considerably lower viscosity at the same concentration. In this manner large differences due to viscosity should be demonstrated.

The results are tabulated in Table 5 and plotted in Figure 4. These data serve to emphasize the fact that the effect of viscosity, if any, is secondary.

VII. <u>The Precision of the Method</u>

The above data were then used to obtain an indication of the precision of the paste-drying technique. Calculation of the rank correlation between the standard deviation and the mean adhesion showed a highly significant correlation, and it cannot therefore be assumed that the standard deviation is independent of the value of the adhesion. Therefore a least squares solution of the regression of the standard deviation on the mean adhesion was prepared. A plot of the regression is shown in Figure 5. However, a regression equation of this type leads to complex statistical calculations. Therefore a new computation was made assuming that the standard deviation regression is

TABLE 5

ADHESION AS A FUNCTION OF STARCH CONCENTRATION

Leather L-97

Potato Starch

Starch Conc. % Wet Basis	Dry Basis	Standard Deviation	Adhesion Grams
1	.87	104.9	425
2	1.74	116.9	763
3	2.61	166.2	1019
4	3.48	146.9	1016
5	4.34	144.9	1078

Tapioca Starch

Wet Basis	Dry Basis	Standard Deviation	Adhesion Grams
2	1.73	75.8	606
3	2.59	107.6	734
4	3.45	116.0	891
5	4.32	95.7	997
6	5.18	152.7	978

Leather L-75

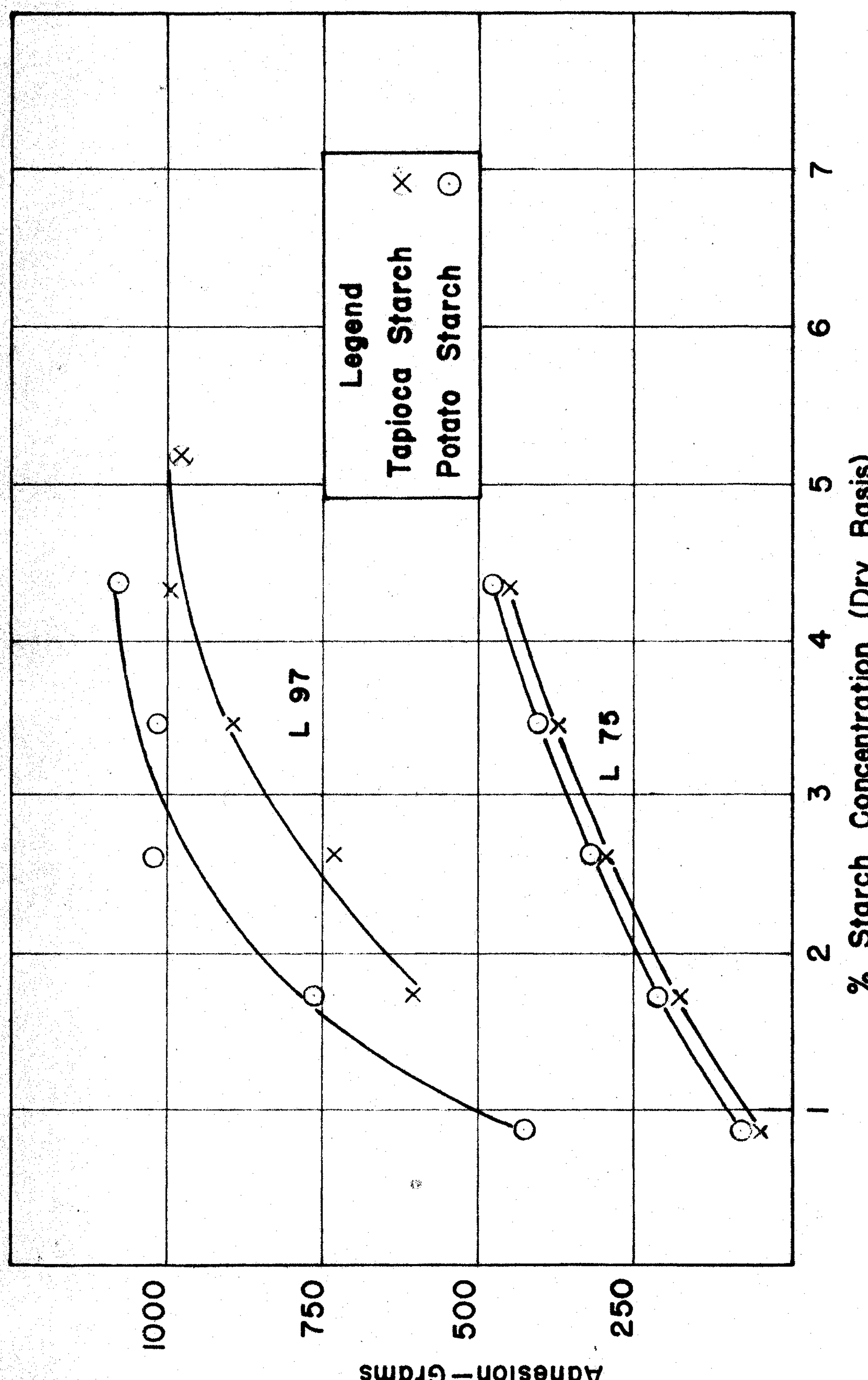
Potato Starch

Wet Basis	Dry Basis	Standard Deviation	Adhesion Grams
1	.87	34.8	82
2	1.74	53.9	216
3	2.61	68.4	320
4	3.48	83.6	411
5	4.34	89.2	481

Tapioca Starch

Wet Basis	Dry Basis	Standard Deviation	Adhesion Grams
1	.86	37.1	52
2	1.73	77.7	180
3	2.59	63.55	301
4	3.45	75.5	377
5	4.32	77.1	455

FIGURE 4



ADHESION vs % STARCH CONCENTRATION

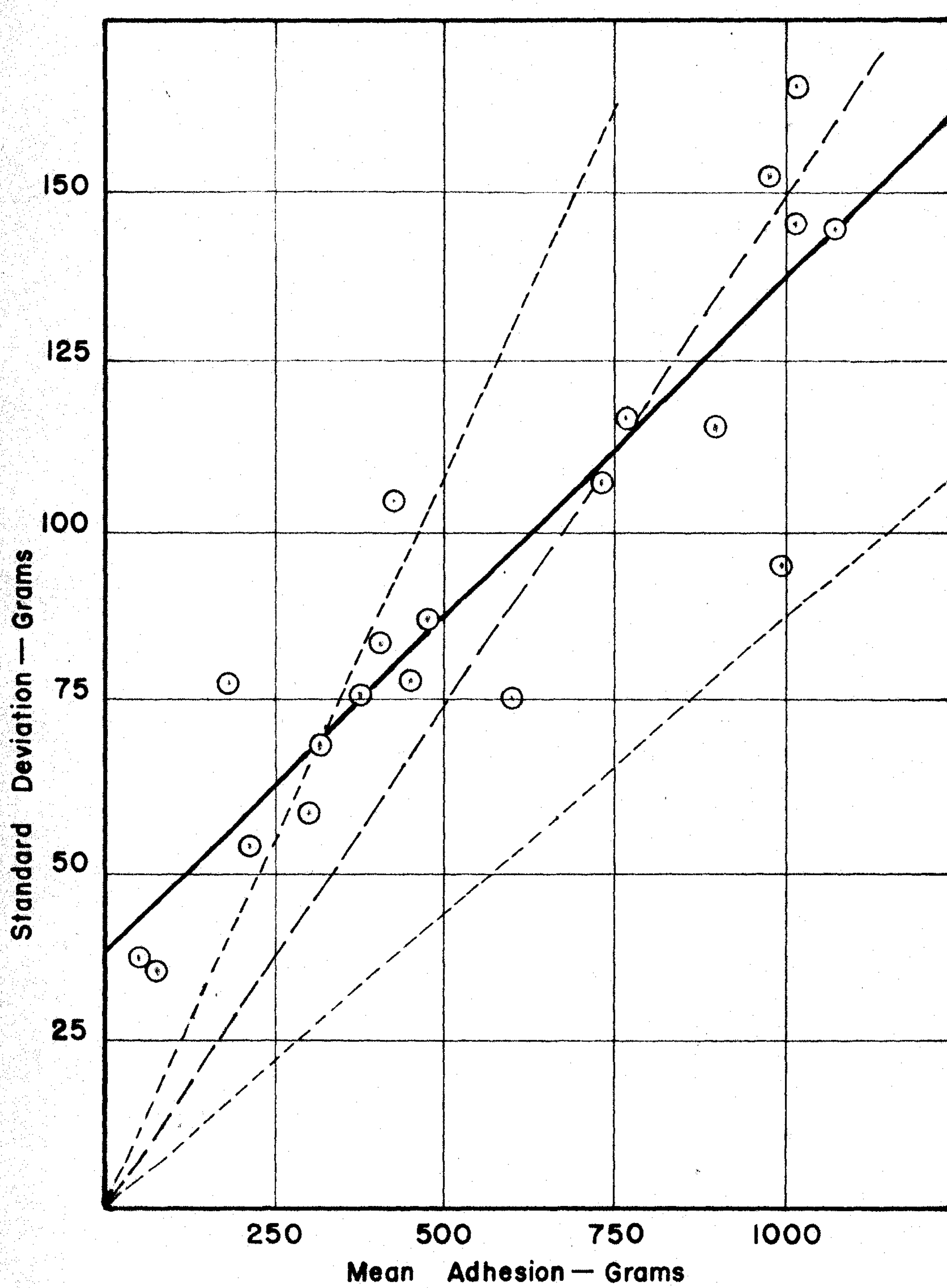


FIGURE 5

PLOT OF ADHESION vs STANDARD DEVIATION

linear and passed through the origin; that is, σ/M (the coefficient of variation) is a constant. This line is plotted in Figure 5. The validity of this assumption was tested by means of the F test. The reasoning leading to this test can best be shown by the following discussion.

If samples are drawn in groups of 16 from a normally distributed population having a certain standard deviation σ, estimates of σ made from the individual groups of 16 samples will show a certain variability due to sampling fluctuations alone. By means of the χ^2 test the range of 99 per cent of the estimates of σ can be computed.

In the problem at hand the true σ of the population is unknown but an estimate made from 320 determinations in groups of 16 is available. By means of the F test the range of estimates of σ can be calculated compared to the estimate prepared from 320 determinations.

Lines were erected on the chart of Figure 5 to show the expected range of estimates of σ if drawn from a population whose coefficient of variation estimated to be 15 per cent. These lines show the assumption to be invalid only in the range below 250 grams adhesion. The utility of this assumption will be shown from the following discussion.

Having estimated the standard deviation of the method to be 15 per cent, a simple calculation will show the differences between samples which the method will detect. Here we shall use the familiar t-test, from Snedecor (14), page 77.

$$t = \frac{D}{\sqrt{\frac{2s^2}{n}}}$$

D = Difference of means of two random samples

s^2 = Variance of each sample

If we divide both numerator and denominator by M, the mean value of either since we are testing the hypothesis that $M_2 - M_1 = 0$

$$t = \frac{D/M}{\sqrt{\frac{2}{n}\frac{s^2}{M^2}}}$$

$\sqrt{\frac{s^2}{M^2}}$ = C, the coefficient of variation

$$t = \frac{(D/M)^2}{\frac{2}{n} C^2}$$

and $$n = \frac{2t^2 C^2}{(D/M)^2}$$

now D/M = Relative difference between samples

and $\frac{C}{D/M}$ Gives the ratio of the relative standard deviation to the relative difference between sample means.

We make this ratio as large as we please, but the number of samples required will increase correspondingly. To keep the number of samples within reasonable limits, let us assume that a relative difference (D) of less than the coefficient of variation (C) cannot be established.

$$n = 2t^2(1)^2$$

This equation must be solved by approximation.

For 16 samples in each group and t at the 1 per cent level for 30 degrees of freedom

$$n = 2x(2.750)^2 \times (1)^2 = 15+ \text{ samples}$$

Therefore, with two groups of data, each comprising 16 determinations, a relative difference equal to the coefficient of variation can be established unless a one-in-a-hundred chance has occurred. To establish a difference of one half this value would require nearly 60 samples in each group.

There is one final question to be considered in the development of a new technique. The question is how much could the precision of the method be improved if further effort were to be expended. In considering the paste-drying technique it is useful to compare the precision of the method with the precision of other physical tests of leather. Present indications are that the precision is at least as good as the precision of any other physical test for leather. It would not seem logical to assume that the technique for measuring adhesion can be refined to any greater degree than other physical measurements of the properties of leather.

VIII. Effect of Moisture Content of Samples

Preliminary studies showed that the chosen blotting technique stabilized the moisture content of the leather samples at approximately 60 per cent, with a range of value of from 57 to 63 per cent. In order to study the effect of moisture content of the leather on its final adhesion, a series of replicate samples of leather L-97 were paste dryed over a range of moisture levels. Moisture was determined by, first, weighing the wet leather immediately before coating with adhesive; and, second, drying the samples overnight in vacuum at 75°C. and weighing, after the samples were removed from the pasting plate.

The data are tabulated on Table 6 and plotted in Figure 6. A rank correlation was calculated to establish the presence or absence of a significant correlation between adhesion and moisture content. The computation shows a highly significant correlation. A least squares calculation of the regression was calculated. The regression line is shown in Figure 6.

The regression equation shows that, of the leathers studied, the adhesion increases 10 grams for a one per cent moisture decrease. In view of the small magnitude of the correction and the fact that it was obtained at only one adhesion level, the correction was neglected.

IX. Change of Adhesion with Time of Storage of Samples

Studies were made of the changes that take place in the adhesive character of the leather on storage. This

TABLE 6

ADHESION AS A FUNCTION

OF MOISTURE CONTENT OF LEATHER

% Moisture	Adhesion Grams	% Moisture	Adhesion Grams
53.5	650	60.7	350
54.3	550	60.3	400
54.4	625	61.0	375
54.4	550	61.3	400
54.8	600	61.2	450
55.0	400	61.3	450
55.2	575	61.4	350
55.9	450	61.4	500
56.5	450	61.3	250
56.9	375	61.5	450
57.0	500	61.7	500
57.0	550	61.8	300
57.3	450	61.9	300
57.5	400	62.0	375
59.1	450	62.0	300
59.2	375	63.1	325
58.6	575	66.7	525
58.7	450	67.3	250
58.8	425	67.4	450
59.4	500	67.5	400
59.7	525	67.5	350
59.7	450	57.5	200
59.9	350	67.6	500
59.5	275	67.7	525
60.0	275	67.9	575
60.2	350	67.9	400
60.2	450	68.0	375
60.5	400	68.2	350
60.6	450	69.0	500
60.8	375	69.4	450
60.8	400	71.1	300
60.8	425	71.1	400

L-75 Leather

3% Potato Starch Pastes

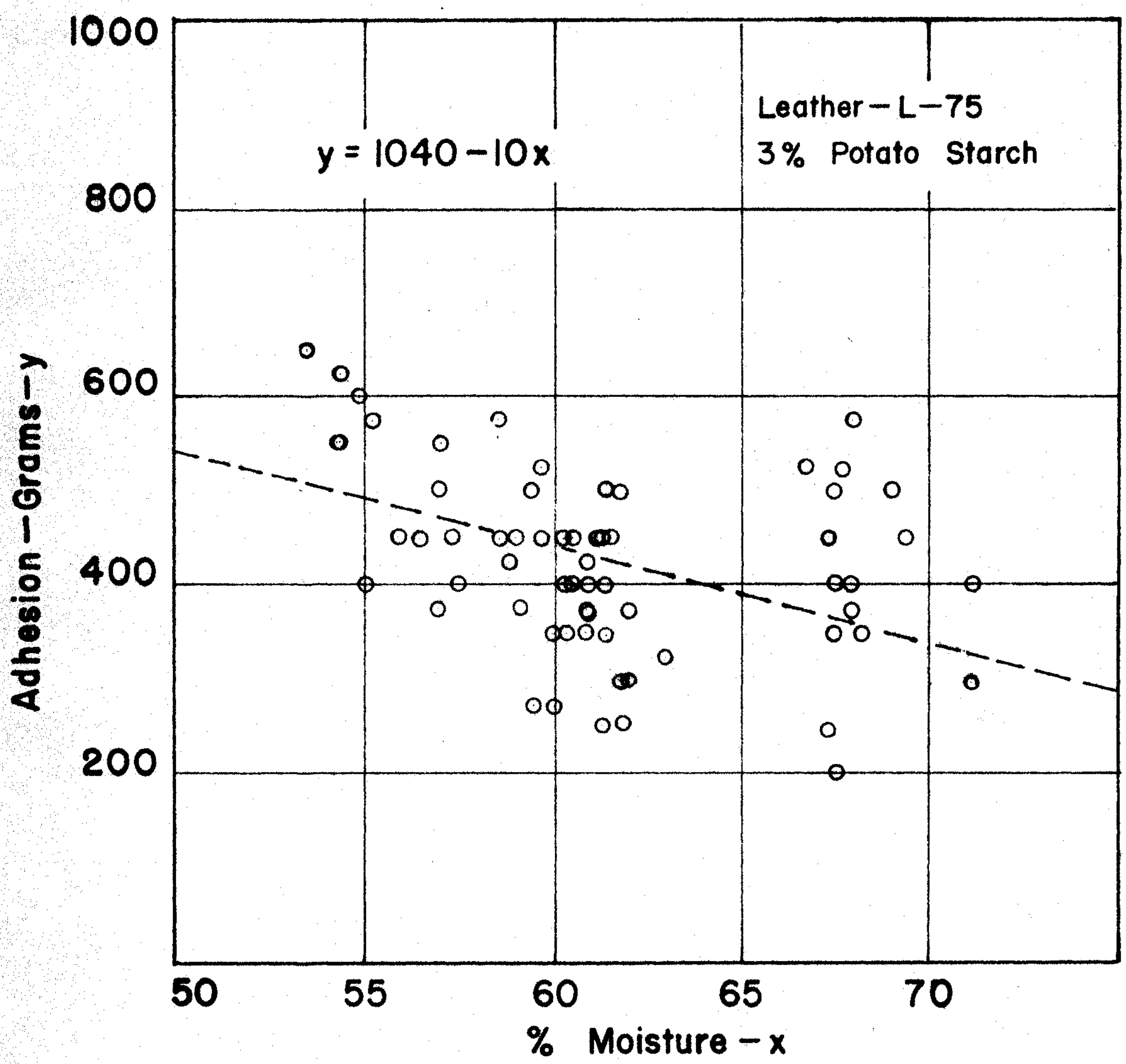


FIGURE 6

PLOT OF % MOISTURE vs ADHESION

was necessary because some of the projected studies would run over a period of several weeks.

Groups of replicate samples of L-75 leather were paste dried at intervals of a few days to several weeks. The results are plotted in Figure 7 and tabulated in Table 7. The results indicate that adhesion may increase rapidly during the early days of storage but that after a period of about thirty days storage, a relatively stable value is attained.

Study of the Effect of Some Leather Components on its Adhesive Character

A. Chemical Analysis of Leather Samples

Reports from the leather industry tended to indicate that dyeing with basic dyes yielded leathers of somewhat lower adhesion than did dyeing with acid or direct dyes. Because of this fact it was felt that correlation of the chemical analyses of the leathers with their adhesive character would prove of value. It was also felt that chemical analysis of the leather in the immediate vicinity of the grain surface would be of greater value than analyses of the gross leather samples.

In preliminary studies, layers of about 100 microns thickness were removed from the grain surface of leather samples by means of a United Shoe Machinery Co. Model A splitting machine. Layers of less than 75 microns or

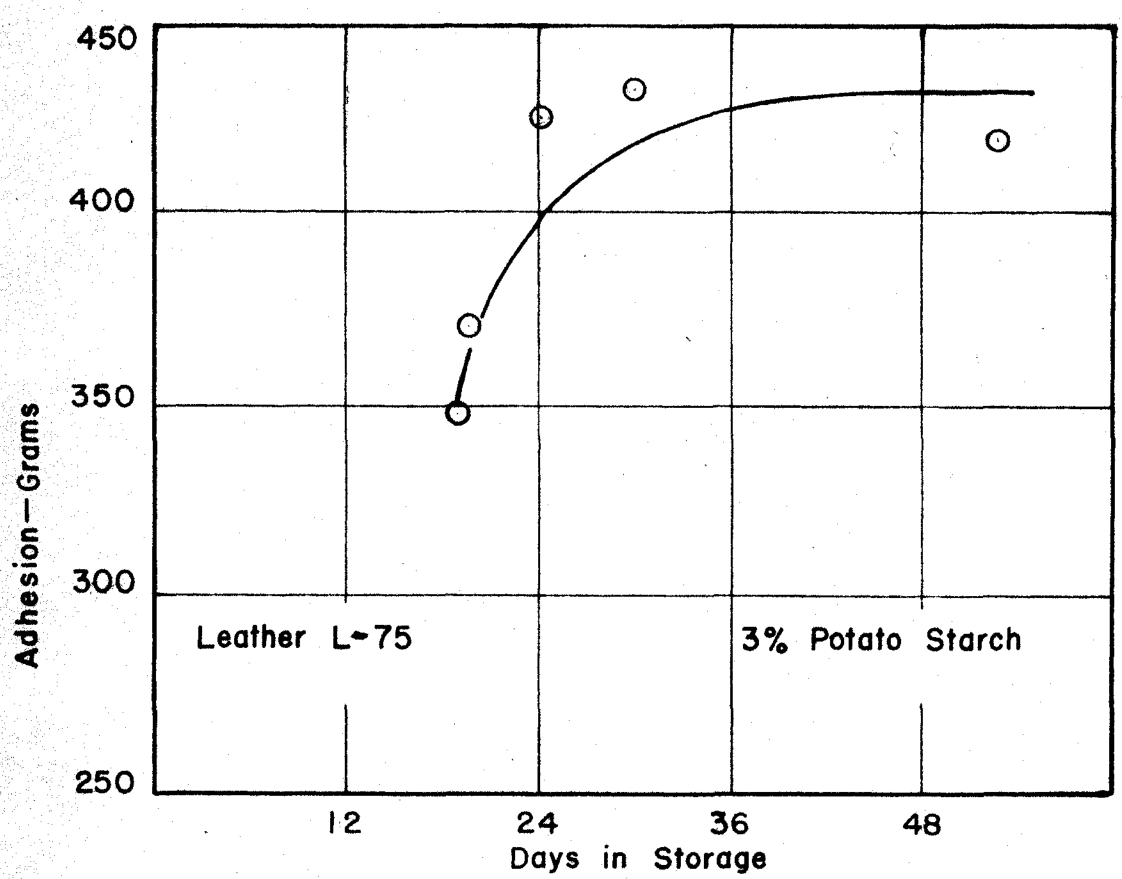
TABLE 7

THE CHANGE OF ADHESION

WITH DURATION OF STORAGE OF LEATHER SAMPLES

Days in Storage	Adhesion Grams
19	348
20	372
24	425
30	433
53	420

FIGURE 7



PLOT OF ADHESION vs STORAGE

more than 125 microns were rejected.

Previous histological studies by Roddy and Koppenhoefer (15) and Roddy (16) showed that the deposition of both chrome and lipid material was fairly uniform throughout the first 100 to 150 microns of the epidermal area. Therefore, as a first approximation slight variations in the thickness of the grain layers should affect the chemical analysis but little. Later studies will show that for the lipid determinations the assumption is valid.

In all of the work 12 pieces each 4" x 6" in size were reserved from each lot of leather. Layers of 100 microns thickness were removed from the grain surface, dried in air, ground in a micro Wiley mill and made into a composite sample for chemical analysis. Allowing for some spoilage during the splitting operation, sufficient sample was obtained for a satisfactory chemical analysis.

With all of the leathers studied, analyses of both the gross leather and the grain split were made. Samples for the analysis of the gross leather were obtained from the scraps remaining after cutting the paste-drying test pieces.

Moisture, nitrogen, chrome oxide, and fat were determined for both the gross and grain samples. The analyses of the gross samples were carried out according to the official methods of the American Leather Chemists Association (17), with the following exceptions:

Moisture was determined by drying 18 hours at 75°C. in vacuum. Fat was determined by means of an 8-hour extraction with petroleum ether and a subsequent 8-hour extraction with ethyl ether. According to Koppenhoefer (18) ethyl ether extracts all the free oil.

The determinations of the constituents of the grain layers were made by appropriate semi-micro modifications of the macro procedures. Moisture was determined by means of a semi-micro method using 200 to 300 milligram samples. Nitrogen was determined by means of the standard Kjeldahl technique used at the Tanners' Council Laboratory, employing 300 milligram samples. Cr_2O_3 was determined by means of a modification of the A.L.C.A. perchloric acid method (17), using 300 milligram samples and one-fiftieth normal thiosulfate. The full macro 10 milliliters of perchloric acid were used, and the oxidized samples were diluted to 200 ml. as is the macro procedure. The sodium thiosulfate was standardized before each set of determinations by means of one-fiftieth normal $K_2Cr_2O_7$. In order to check the semi-micro procedure, a fairly large sample of leather was prepared and analyzed by means of both the macro and semi-micro methods. Table 8 summarizes the results. Examination of these results show that the semi-micro procedure gives the same results as the macro method.

Fat was determined in the same manner as the gross samples, using micro extractions and 200 milligram samples.

TABLE 8

SUMMARY OF ANALYTICAL RESULTS

STANDARDIZATION OF SEMI MICRO PROCEDURE

FOR DETERMINATION OF Cr_2O_3

10 ml. $HClO_4$ used.

Leather 1

Ashing Procedure:

Micro		Macro	
3.48		3.50	
3.49		3.52	Aver. 3.51
3.52			
3.53	Aver. 3.51		

Leather 2

Wet Ashing:

Micro		Macro	
4.06		4.02	
4.02		4.02	Aver. 4.02
4.06			
4.10			
4.02	Aver. 4.05		

Blanks were carried with each set of determinations.

In order to study the possibility that small quantities of extractable material were absorbed by the leather during the splitting operation, the following experiments were performed. Samples of L-75 leather were cut into pieces of convenient size and exhaustively extracted with petroleum ether in Soxhlet extractors. After extraction a portion of the leather was removed, ground in a Wiley mill, and re-extracted with petroleum ether to determine the residual fat remaining. A second portion of the extracted leather was removed and split into a number of layers by means of the United Shoe Machinery Co. splitting machine. The layers were collected, ground in a micro Wiley mill and extracted with petroleum ether as before. Any increase in extractable material was taken as fat absorbed during the splitting operation. The results are shown in Table 9. The data indicate that a negligable amount of fat is absorbed.

B. Correlation of Adhesive Character with Chemical Analysis

In order to study the effect of type of dyestuff on the pasting character of leathers, preliminary samples consisting of three shoulders each of acid, basic, and direct dyed leathers were obtained. These leathers were mordanted with 1 per cent vegetable tanning material and were fatliquored with commercial sulfated oils containing

TABLE 9

AMOUNT OF FAT ABSORBED BY LEATHER
DURING SPLITTING OPERATION

Defatted leather before splitting:		
% Fat -- dry basis	0.24%	
	0.26%	Av. 25%
Defatted leather after splitting:		
% Fat -- dry basis	0.33%	
	0.36%	Av. 35%
Increase in fat content attributable to splitting operation:		0.10%

raw oil.

Employing procedures already outlined, the adhesion of the three leathers were compared. Moisture, nitrogen, chrome oxide, and fat content were also determined for the gross leathers and grain splits. The results of these experiments are tabulated in Table 10.

Examination of the paste-drying test data show a tendency toward a lower adhesion on the part of the basic dyed leathers. The chemical analyses, on the other hand, show no significant differences in the chrome content of the leathers and a much greater fat content in the eip-dermal area of the basic dyed leathers.

In order to study these effects in greater detail a second series of leathers was obtained from the tannery. As with the previous set of leathers these shoulders were divided into groups of three shoulders each, dyed with acid, basic, and direct dyes, and were vegetable mordanted as before. However, in these studies each of the three major groups were divided into four sub-groups. Each sub-group was to contain different quantities of fatliquor. The following table shows the sample scheme requested from the tannery:

Acid Dye		Basic Dye		Direct Dye	
Fatliq. Content	Code	Fatliq. Content	Code	Fatliq. Content	Code
3	A3	3	B3	3	D3
5	A5	5	B5	5	D5
8	A8	8	B8	8	D8
12	A12	12	B12	12	D12

TABLE 10

CHEMICAL ANALYSES

ACID, BASIC AND DIRECT DYED LEATHERS

LOT I

	% N	% Hide Subs.	Pet. Ether	Ethyl Ether	Total	Total on Hide Subs.	Chrome %	Chrome Hide Subs.
Acid Dye								
Gross	14.25	80.02	4.15	.37	4.52	5.65	3.73	4.66
Grain	11.25	63.22	9.94	.56	10.50	16.62	3.63	5.74
Basic Dye								
Gross	12.60	72.43	10.95	.65	11.60	16.02	3.23	4.46
Grain	9.64	54.30	21.11	.48	21.59	39.76	2.93	5.40
Direct Dye								
Gross	14.35	80.67	3.89	.36	3.50	4.34	3.79	4.70
Grain	11.53	64.82	8.10	.40	8.50	12.11	3.74	5.77

When these leathers were received at the laboratory, analyses of the total samples and the grain splits were performed. Paste-drying experiments were also carried out using groups of 16 samples for each experiment. These experiments were performed using both 1 per cent and 3 per cent potato starch pastes (sir dry basis). The analytical data are tabulated in Table 11.

A preliminary plot of the adhesion data as a function of the per cent fat on the hide substance (per cent nitrogen x 5.62) was prepared. An examination of the curves showed that the results obtained for the D-8 leathers with the 3 per cent starch paste might be discordant. Accordingly, two additional groups of D-8 samples were paste dried using 3 per cent starch paste. The new values show somewhat better agreement with the rest of the data. Further examination of the plot showed poor agreement for the acid dyed leathers paste dried with 1 per cent starch pastes. These acid dyed leathers felt somewhat firmer at all fatliquor levels than did either the basic or direct dyed leathers. Because of the greater firmness it was felt that increased softening of the samples before paste drying might yield more consistant results. Therefore the entire acid dye series was repeated using both 1 per cent and 3 per cent starch pastes. In the repeat series the samples were flexed ten times in each direction instead of twice as

TABLE 11

CHEMICAL ANALYSES -- ACID, BASIC AND DIRECT DYED LEATHERS

Gross Sample

Sample No.	Mean % Hide Subs.	Mean % Fat Pet.Ether	Mean % Fat Et.Ether	Mean % Fat Total	Mean % Fat on Hide Subs.	Mean % Ash	Mean % Cr_2O_3	Mean % Cr_2O_3 on Hide Subs.
A-3	80.85	4.10	.32	4.42	5.47	4.60	3.73	4.61
A-5	82.35	4.64	.21	4.85	5.89	4.42	3.61	4.27
A-8	81.39	5.79	.29	6.08	7.48	4.45	3.58	4.40
A-12	79.45	7.14	.39	7.53	9.50	4.55	3.54	4.45
B-3	82.97	3.56	.48	4.04	4.87	4.59	3.72	4.48
B-5	83.84	4.77	.37	5.14	6.14	4.58	3.69	4.40
B-8	80.18	5.84	.88	6.72	8.37	4.68	3.66	4.56
B-12	79.44	7.08	.98	8.07	10.02	4.47	3.48	4.39
D-3	83.72	2.35	.46	2.81	3.36	4.88	3.96	4.73
D-5	85.07	2.43	.48	2.91	3.42	4.60	3.80	4.46
D-8	82.80	4.12	.65	4.77	5.76	4.58	3.71	4.48
D-12	78.76	6.14	.73	7.02	8.91	4.52	3.57	4.54

Grain Split

Sample No.	Mean % Hide Subs.	Mean % Fat Pet.Ether	Mean % Fat Et.Ether	Mean % Fat Total	Mean % Fat on Hide Subs.	Mean % Ash	Mean % Cr_2O_3	Mean % Cr_2O_3 on Hide Subs.
A-3	62.29	9.40	.75	10.1	16.2	5.52	4.00	6.43
A-5	60.76	11.0	.90	11.9	19.6	5.58	3.94	6.48
A-8	58.55	14.1	1.12	15.2	26.0	5.13	3.65	6.23
A-12	54.80	18.0	1.64	19.6	35.8	5.25	3.37	6.15
B-3	59.99	9.24	1.11	10.4	17.3	5.59	3.66	6.09
B-5	59.56	10.8	1.17	12.0	20.1	5.38	3.53	5.93
B-8	57.6	13.1	2.05	15.1	26.2	5.26	3.28	5.70
B-12	58.6	13.75	1.61	15.4	26.3	5.33	3.33	5.69
D-3	62.54	7.68	.79	8.48	13.6	5.64	4.28	6.85
D-5	63.08	9.18	1.40	10.6	16.8	5.62	4.31	6.83
D-8	58.93	11.3	1.70	13.0	22.0	5.63	3.95	6.83
D-12	54.13	17.5	2.18	19.7	36.4	5.49	3.51	6.49

in the standard procedure. The results of these experiments show little change at the 3 per cent starch level and considerable change at the 1 per cent level. The data are tabulated in Table 12 and plotted in Figure 8.

In Figure 8 the best eye-fitted curve was drawn among the points. This curve was then rectified by graphical differentiation to determine the form of the equation. The final equations are shown in Figure 8.

In order further to check the precision of the paste-drying method, "least square" solutions of the regression of standard deviation as a function of adhesion were prepared for both the 1 per cent and 3 per cent starch data. These are plotted in Figure 9. For the 3 per cent starch data the equation is very similar to that obtained previously. However, for the 1 per cent starch data the standard deviation increases much more rapidly. Because of the rapid increase in standard deviation and the low adhesion values obtained, no conclusion may be drawn from the 1 per cent starch paste data.

C. Confirmatory Experiments

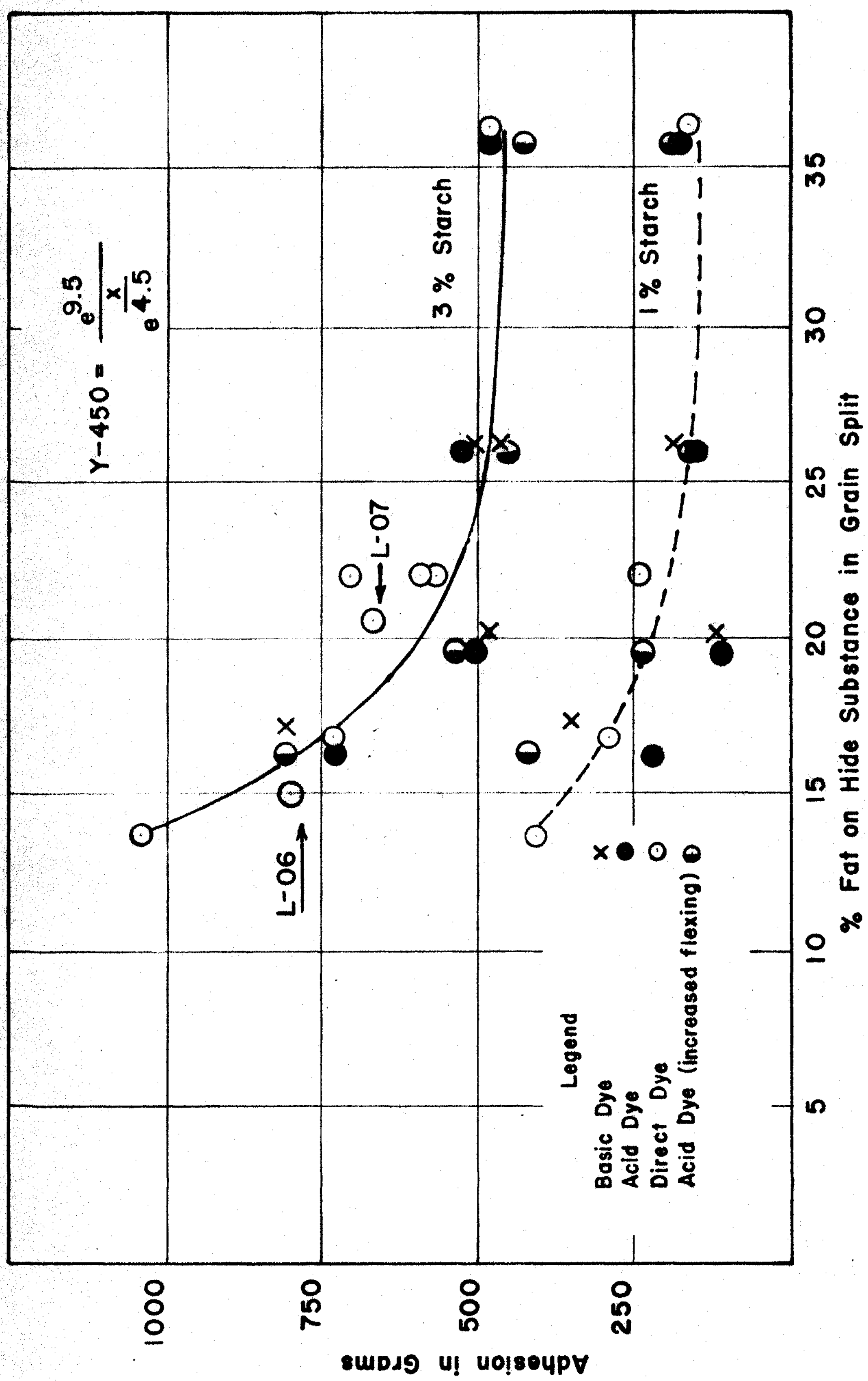
Examination of the 3 per cent starch data indicated that a real correlation existed between the adhesion obtained and the amount of extractable fat present in the grain split. In order to confirm this correlation the following experiments were performed: Two undyed shoulders having a high fatliquor level were obtained. The leather

TABLE 12

ADHESION VS. PER CENT FAT IN GRAIN SPLIT

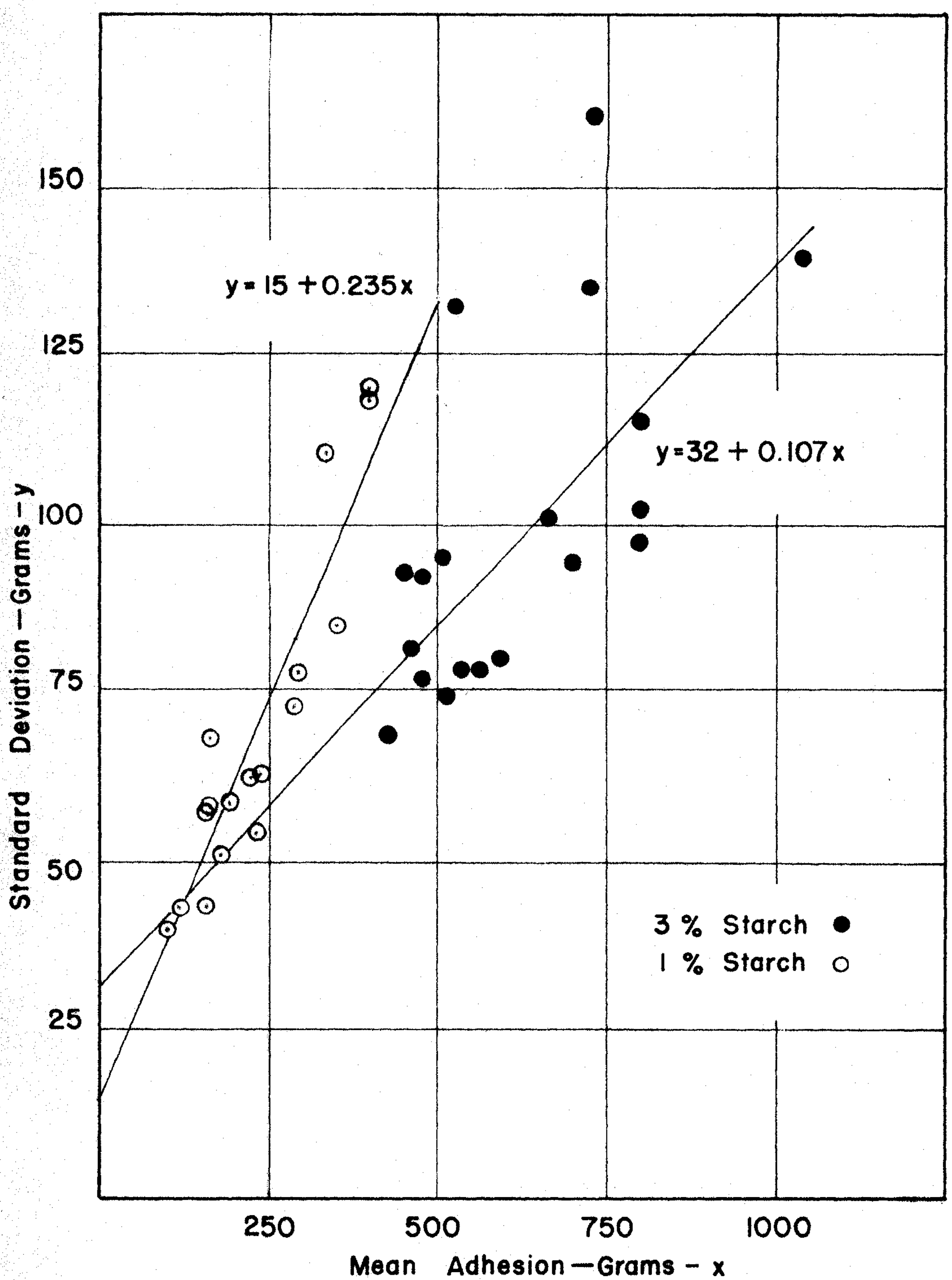
Sample	% Fat in Grain Split on Hide Subs.	Adhesion (Grams) 1% Starch	Std. Devia.	3% Starch	Std. Devia.	3% Starch Log Adhesion
HFA-3	16.2	422	120.0	803	102.5	2.905
5	19.6	236	54.7	537	78.5	2.730
8	26.0	169	63.6	450	93.1	2.653
12	35.8	198	63.6	425	63.2	2.628
A-3		223	62.2	731	161.1	2.864
5		106	40.3	506	95.3	2.704
8		158	68.7	528	132.8	2.723
12		178	51.5	481	77.1	2.682
D-3	13.6	406	118.0	1041	140.4	3.017
5	16.8	290	72.4	728	136.7	2.862
8	22.0	242	63.1	705	94.7	2.848
				569	77.8	2.755
				591	80.0	2.772
12	36.4	163	43.7	481	63.6	2.682
B-3	17.3	350	85.1	807	97.8	2.907
5	20.1	117	43.4	481	92.2	2.682
8	26.2	155	57.2	514	74.6	2.711
12	26.3	177	58.7	469	81.4	2.671

FIGURE 8



PLOT OF ADHESION vs % FAT IN GRAIN SPLIT

FIGURE 9



PLOT OF ADHESION vs STANDARD DEVIATION

was analyzed and a paste-drying experiment was performed using 16 samples and a 3 per cent starch paste. Additional paste-drying samples were then treated with three changes of acetone over a period of ten days. At the end of the ten days the samples were removed to several changes of water to remove the acetone. A group of 14 acetone treated samples was paste dried without further treatment. Another group of 14 acetone treated samples was coated on the grain surface with a 30 per cent emulsion of (Tanoyl 1746) a sulfated oil product and paste dried. The results are tabulated in Table 13.

The results show that the acetone treatment increased the adhesion considerably while a film of sulfated oil placed on the surface of the acetone treated leather reduced the adhesion nearly to its original value.

D. The Effect of Chrome Content

To study the effect of chrome oxide content of leather on adhesion, two three-shoulder groups of chrome tanned, acid dyed, vegetable mordanted leathers were obtained. One group was to have a low chrome oxide content while the other was to have a high chrome oxide content. Both samples were supposed to have approximately the same fatliquor content. These leathers were analyzed and paste-drying tests performed using both 1 per cent and 3 per cent starch. The data are tabulated in Table 14 and the results of the paste-drying experiment plotted in Figure 8.

TABLE 13

CHANGE OF ADHESION OF UNDYED LEATHER ON ACETONE TREATMENT AND SUBSEQUENT TREATMENT WITH EMULSION OF SULFATED OIL

Untreated samples.................	204 grams
Acetone treated samples...........	1614 grams
Acetone treated, subsequently coated with an emulsion of sulfated oil prior to paste drying...	256 grams

TABLE 14

SUMMARY OF CHEMICAL ANALYSES AND PASTE DRYING EXPERIMENTS

LOW AND HIGH Cr_2O_3 CONTENT LEATHERS

L-06 Leather

	% H_2O	% Ash	% Hide Subs.	% Cr_2O_3	% Cr_2O_3 Hide Subs.	% Fat Pet.Ether	% Fat Et.Ether	Total % Fat	Total % Fat on Hide Subs.
Gross	10.45	4.22	84.3	3.63	4.31	3.30	0.44	3.74	4.44
Grain	9.02	5.50	66.4	4.02	6.05	8.99	1.10	9.96	15.0

Adhesion (1% Potato Starch) -- 339 grams
Adhesion (3% Potato Starch) -- 800 grams

L-07 Leather

	% H_2O	% Ash	% Hide Subs.	% Cr_2O_3	% Cr_2O_3 Hide Subs.	% Fat Pet.Ether	% Fat Et.Ether	Total % Fat	Total % Fat on Hide Subs.
Gross	11.32	7.35	75.0	6.93	9.23	5.33	0.68	6.01	8.02
Grain	8.89	8.08	58.3	6.63	11.4	10.55	2.40	11.95	20.5

Adhesion (1% Potato Starch) -- 294 grams
Adhesion (3% Potato Starch) -- 665 grams

TABLE 15

SUMMARY OF CHEMICAL ANALYSES

	% Ash	% Hide Subs.	% Cr_2O_3	% Cr_2O_3 on Hide Subs.	% Fat Pet.Ether	% Fat Et.Ether	Total % Fat	Total % Fat on Hide Subs.
L-75 Leather								
Gross	4.70	82.6	3.86	4.68	5.36	0.54	5.90	7.14
Grain	5.47	68.7	3.96	5.76	10.44	1.06	11.5	16.7
L-97 Leather								
Gross	4.76	86.6	4.34	5.02	3.40	.62	4.02	4.64
Grain	4.68	76.0	4.18	5.50	6.52	1.00	7.52	9.90
Undyed Leather								
Gross	4.60	75.6	3.96	5.24	12.03	0.91	12.94	17.1
Grain	4.72	59.2	3.95	6.68	21.6	1.8	23.4	39.4

Results reported on dry basis.

DISCUSSION OF RESULTS

Effect of Starch Viscosity on Adhesion

In the experimental portion of this thesis the statement was made that the effect of starch viscosity on adhesion is secondary. Consideration of the viscosity, concentration relationships of the tapioca starch, and the potato starch pastes will show this to be true. The tapioca starch pastes used had a much lower viscosity than the potato starch pastes, while the measured values of adhesion were only slightly different. The adhesion values obtained with the tapioca starch pastes are in every case lower than those obtained with the potato starch pastes. The difference, however, is not nearly sufficient to compensate for the differences in viscosity.

The same data serve to emphasize the apparent nature of the measurements. This is shown with the L-97 series of leathers which had a high adhesion and showed damage to the grain surface at all starch concentrations. On the other hand, the L-75 samples show no grain damage at any starch paste concentration.

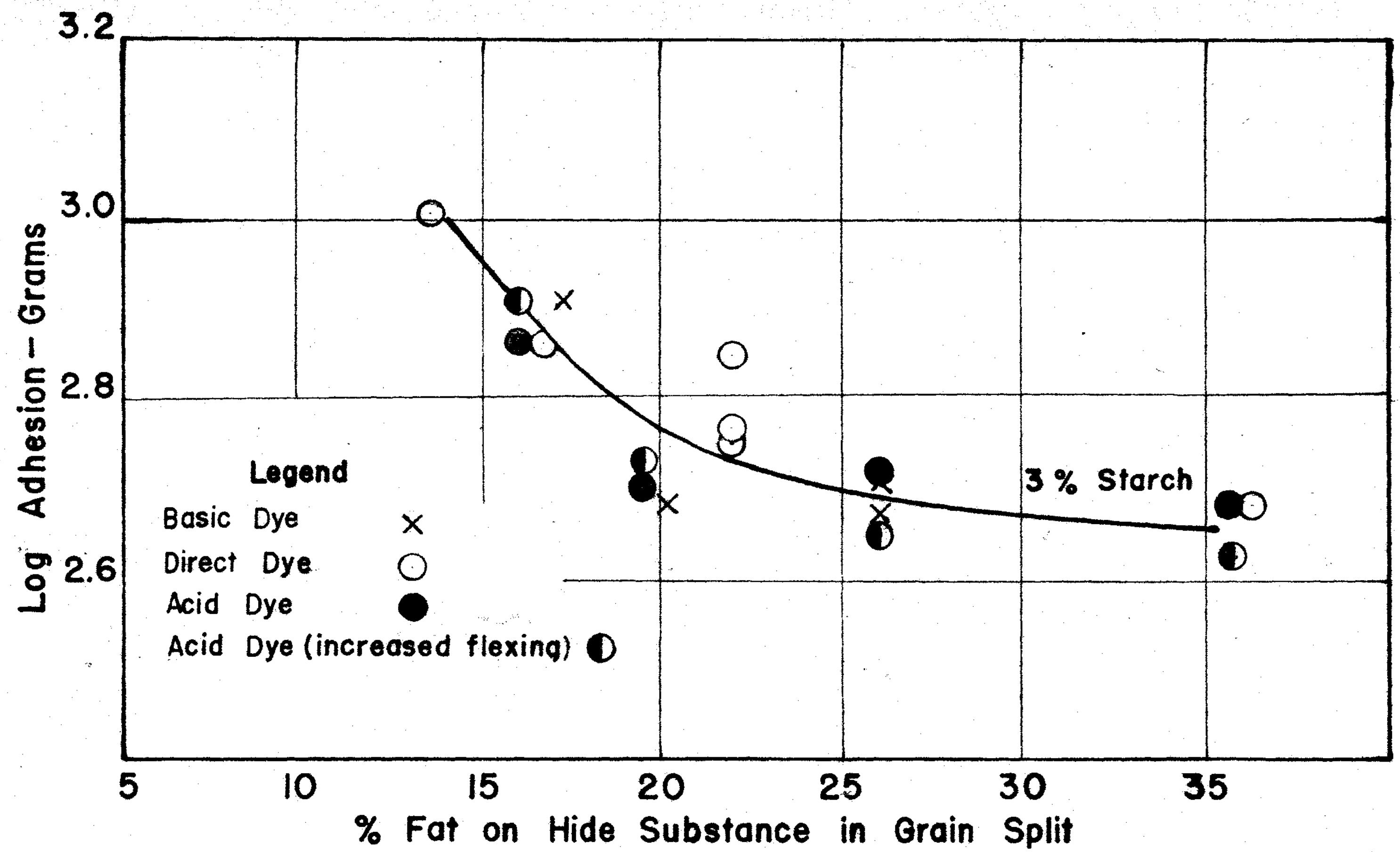
Precision of the Paste-Drying Method

The precision index of the paste-drying method was developed before further work could be undertaken. Examination of Figure 11 reveals that the equation relating the standard deviation with the adhesion for 3 per cent starch is very similar to that obtained previously. This adds considerable evidence to the validity of the method. However, for the 1 per cent starch pastes the standard deviation increases much more rapidly. Because of the rapid increase in the standard deviation and the low adhesion values obtained, no conclusions may be drawn from the 1 per cent starch paste data. The 1 per cent starch paste data demonstrate that only a comparatively narrow range of starch paste concentrations are useful for the study of the adhesive character of leathers. A range must be selected to give maximum differentiation of the values with the lowest relative standard deviation. The optimum starch paste concentration is not far from the 3 per cent level.

The Correlation Between the Fat Content of the Grain Surface and the Adhesive Character of the Leather

In order to present the information in Figure 8 in such a form that all of the points would have about the same precision, the data were replotted using the logarithms of the adhesion versus per cent fat, as shown in Figure 10. The validity of the assumption of constant coefficient of variation shows that the plotted data presented has the required uniform precision. The data indicate a positive correlation between the variables. The correlation is corroborated by the confirmatory experiments presented.

FIGURE 10



PLOT OF LOG ADHESION vs % FAT IN GRAIN

These experiments demonstrate that the adhesive character of leather can be controlled over rather wide limits by employing methods which are known to alter the fat content of the leather.

The data also indicate that the effect produced by different types of dyestuff is negligible. Examination of the data shows that the measured adhesion of leathers dyed with different types of dyestuff differ very little from the curve and from each other.

The adhesion data obtained with the leathers having different chrome oxide contents are plotted in Figure 8, cognizance being taken of the different fat contents of these leathers. Calculations show that in neither case do the data differ significantly from the curve previously obtained. With the leathers studied, therefore, the effect of their chrome oxide content, if any, is small.

When all of the data are considered as a unit, certain anomalies are apparent. The 3 per cent potato starch data of the L-97 and L-75 leathers are plotted in Figure 8 for comparison. It is evident that in the range between 17 and 22 per cent fat the deviations from the curve are greater than in any other region. This is especially true in the case of the L-75 leathers. A possible explanation would be that in this range enough fatty material is present on the grain surface of the leather to coat all of of the fibers of the leather. If the fatty material acts to decrease the adhesion of the leather by forming a non-adhesive film over the surface of the fibers, then a uniform film of fats on the fibers would lower the measured adhesion to a minimum value. A non-uniform deposition of fat on the grain surface could lead to anomalous results.

CONCLUSIONS AND SUMMARY

An experimental method for measuring the adhesive character of leather when paste dried on glass plates has been developed. An overall precision index of 15 per cent has been obtained for the method. Effective use of the method requires careful standardization of the moisture content, flexibility, and storage time of the leather samples.

A direct positive correlation between the amount of extractable fatty material present in the epidermal area of certain leathers and their adhesive character has been demonstrated. The correlation is not significantly affected by type of dyestuff and amount of chrome oxide present.

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