

FURTHER STUDIES ON FOOT PERSPIRATION AND ITS ACTION ON FOOTWEAR

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(With 1 Figure in the Text)

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INTRODUCTION

Previous experiments (Colin-Russ, 1935, 1940) have shown two principal facts: (1) that foot perspiration is essentially an emulsion in salt solution of sweat and sebum with other organic constituents; (2) that foot perspiration decomposes upper chrome leather and forms Glauber's salts, consequent on the release of ionizable sulphate from the basic chrome tannage.

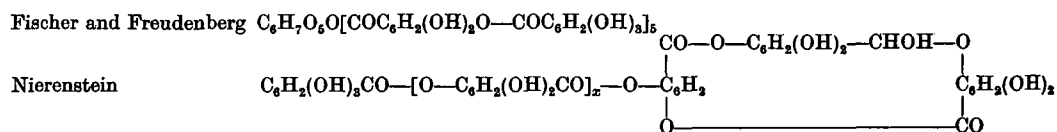
It was mentioned that the work should have an important bearing on the suitability of upper material clothing the foot. Accordingly, the present paper reports the action of foot perspiration under conditions more closely approximating to those of actual wear. Hitherto, accentuated effects were considered of saline and acidic components of perspiration, as well as the general perspiratory action. Now the total effect is studied under the working range of pH corresponding to the normal and pathological functioning of perspiration in the presence of buffered tans. At the same time, due account is taken of variation in the composition of the chrome complex in upper leather tannages.

Tanning material is invariably washed out by perspiration functioning primarily as a solvent on the insoles of footwear, and flexure, coupled with some friction, subsequently works it through the vamps of the upper material, apart from darkening the interior of the shoes. Invariably, judging by the stains left on the fabric vamp-linings, this migration is located mostly at the inner and outer joints, and it is in these regions that perspiration exercises its most frequent disruptive influence in the form of detannization of the upper leather and deposition of salty matter.

In planning the experiments, regard was paid to the amount of washed-out tans from insoles which corresponded to an average weight of upper material and also to securing a sufficient width of pH range by means of a universal buffer. For the latter, a mixed salt was used as devised by Prideaux & Ward (1924) which, by the simple addition of

0.2N HCl or NaOH in a given volume of solution, gave pH values according to the formula $pH = 3.1 \pm 0.1185V$, where V is the volume of acid or alkali.

Concerning the tanning matter which perspiration can wash out of the insole into the vamp under flexure during wear, mixed theoretical and practical considerations applied to the system (perspiration-tannin-buffer-leather) led to the adoption throughout all the experiments of 9.4000 g. tannin (as gallotannic acid) for every 33 g. upper material. The latter weight was an average possibility from a random choice of material taken apart from a men's shoe. The tannin weight was based on two main factors: (1) the insole weight varies more or less about a range roughly twice that of the vamp lasted to it; (2) insoles may contain 15–30% water solubles and often no more than a third of these is washed out, whilst the worn shoe is in good unrepaired condition. Theoretically, then, whether we regard with Fischer (1919) and Freudenberg (1920) the constitution of tannin as a pentadigalloyl glucose or with Nierenstein (1922) as a polydigalloyl-leuco-digallic acid anhydride,



the experiments about to be described can be regarded as studies of the perspiratory action on chrome upper in the presence of about 0.4–3.0 mg. mol. tannin for every 5 g. lot of leather at varying acidities.

EXPERIMENTS AND DEDUCTIONS

(1) General procedure

Three stock solutions were prepared labelled B, T and P:

B. Buffer solution of double strength, so that dilution with equal bulk was required (including any acidic or alkaline addition) to bring to the pH desired according to the formula given in the preceding section.

T. 28.2% *w/v* gallotannin acid as checked by evaporation of an aliquot portion to dryness and confirming constancy of weight after oven-drying at 100° C.

P. Synthetic perspiration as formulated in an earlier paper (Colin-Russ, 1935) but omitting the sulphate constituent and working on a basis of 20 g. cholesterol. For this purpose, 'Hartolan' as a commercially pure and convenient form of cholesterol was obtained. The emulsion should be formed by melting the tallow, cholesterol and phospholipin with the organic acids and briskly stirring, whilst gradually adding the aqueous mixture of urea and inorganic salts at 35° C. Frothing can be eliminated with a few drops of caprylic alcohol.

Several samples of leather (box and willow calf) having chrome oxide contents varying between 2.5 and 6.0% were separately cut into pieces 0.25 cm. sq. Each sample was investigated in 5 g. lots admixed with 50 ml. of B, 5 ml. of T, 10 g. of P and water to make the final volume 100 ml. The main significant item sought for was the sulphate lost by the leather sample and was determined by the method previously described (Colin-Russ, 1940). Chromic oxide losses were found to be small but were nevertheless completed throughout the analytical series. Furthermore, each investigation was

completed with an electrometric determination of the *pH* both initially and finally in the system. The initial *pH* was obtained *before* admixture with the leather, and the final *pH* *after* filtering from the leather.

The effects of the buffer and tannin, combined and separately, were also noted, as these served at the same time as controls in the comparative study of the perspiration influence alone.

All these investigations were conducted at three temperatures, 18, 35 and 100° C., as in previous work. By way of continuity, one of the sampled leathers studied was identical with box calf '613' of Table 1 in my last paper (Colin-Russ, 1940).

Only one strength of perspiration reagent was used throughout the entire work, otherwise the comparison of the data would have been invalidated in view of the increase in detanning power on chrome upper leather with increase in strength of the perspiration solids:

% strength of perspiration	1.0	5.0	10.0	20.0
% loss of ionizable sulphate ('613') based on total =SO ₄	23.85	41.5	57.5	76.5

(2) *The effects at varying temperatures and pH of six different chemical systems on the upper leather*

Experiment 1. With box calf '613'.

The data are given in Table 1. The effects of P alone which had been given in a previous paper (Colin-Russ, 1940) are also included for convenient reference in drawing comparisons. The acidity effect of perspiration is manifest in each system, as, when comparing (P + T + B) and (T + B). These contain the same buffer. Thus, in system 2, the result of

Table 1. *Box calf '613'*

Chrome oxide 2.67%. Basicity 65.9.

Sulphates lost as a percentage of the original total of 2.00%

System ...	With P + T + B			With T + B			With P + B	With B		With P only		
	18	35	100	18	35	100		24	100	18	25	100
1. Loss	20.15	27.20	67.50	16.85	23.40	44.80	69.95	12.74	56.00	1.90	19.50	54.60
Initial <i>pH</i>	2.70	2.70	2.70	3.18	3.18	3.18	2.69	3.26	3.26	2.74	2.74	2.74
Final <i>pH</i>	2.84	2.86	2.94	3.23	3.19	3.04	3.12	3.29	3.38			
2. Loss	25.90	37.85	78.50	36.60	52.00	68.50						With T only
Initial <i>pH</i>	5.20	5.20	5.20	8.52	8.52	8.52						22.65
Final <i>pH</i>	5.20	5.06	4.59	8.34	8.12	6.05						2.86
3. Loss	44.00	55.00	96.50									
Initial <i>pH</i>	8.70	8.70	8.70									
Final <i>pH</i>	8.29	8.13	6.22									

Note. 10.00 ml. *N* NaOH present in system 2. 19.50 ml. *N* NaOH present in system 3.

System no.	Chrome oxide lost as a percentage of the original											
1	0.19	0.19	0.37	0.76	0.76	1.91	3.82	0.38	0.95	0.2	1.5	3.4
2	0.11	0.30	0.37	0.19	0.38	0.82						
3	0.57	0.57	0.94									

adding P is to cause a drop from *pH* 8.52 to 5.20, although the same buffer is present; system 3, however, by the extra addition of alkali and checking electrometrically, provides a comparable set with system 2.

The following conclusions can be drawn:

(1) The greatest loss in ionizable sulphate from the upper and the greatest loss in

chromic oxide, small though the latter may be, occur when perspiration is present, except when tannin is present in the case of the chrome release.

(2) The loss in sulphate, whether perspiration be present or not, increases with the temperature at all *pH* values. Fig. 1 indicates a linear increase for systems of (P + T + B), thus:

$$\text{At } pH \ 8.7, \% \ SO_4 = 0.64 (t - 18) + 44.0,$$

$$\text{At } pH \ 5.2, \% \ SO_4 = 0.64 (t - 18) + 25.9,$$

$$\text{At } pH \ 2.7, \% \ SO_4 = 0.57 (t - 18) + 19.0.$$

(3) In the presence of tans, the influence of perspiration of similar *pH* in releasing sulphate is distinctly enhanced, and this is true even though it is observed that the buffering agent itself has a similar decomposing action.

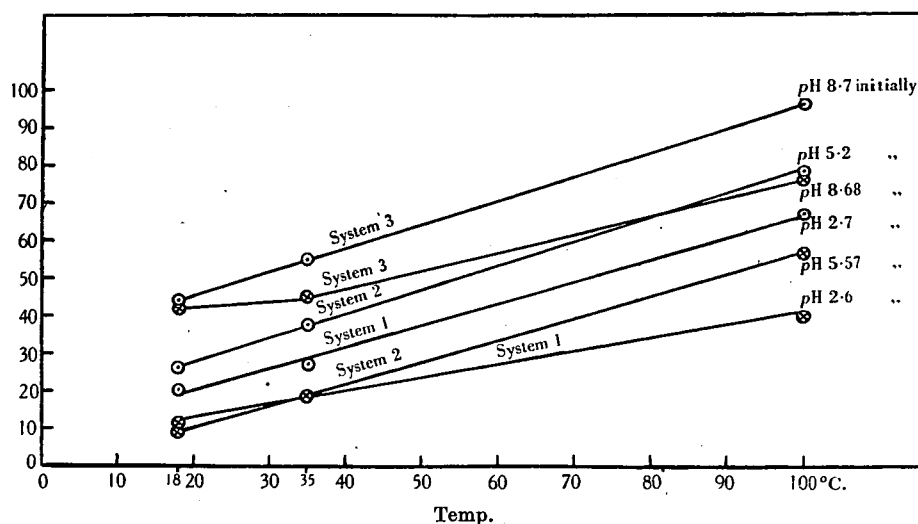


Fig. 1.

(4) When the initial *pH* is about 3 or less, the final *pH* is slightly increased at the end of 1 hr. When the initial *pH* is above the isoelectric point and even alkaline, the final *pH* decreases, and the decrease is greatest at 100° C.

(5) At lower temperatures (18–35° C.) but at higher *pH* values, buffered tans tend to decompose upper leather a little further than when perspiration is also present, unless the latter is neutralized to a similar *pH*. This means that where a person's foot perspiration is merely profuse and fairly neutral, insertion of foot powders inside the shoes, such as borated compounds (British Boot, Shoe and Allied Trades Research Association, 1935), could be deleterious to the life of the upper leather even if the amount of borax is too small to spue out. Alternatively, buffering the vegetable tannage of the insole with so-called protective salts to prevent discoloration or oxidation, embrittled fibres, etc., would promote decomposition of the uppers if the perspiration moisture is sufficiently active.

(6) The decomposing action of perspiration increases with the *pH* of the system whatever the temperature.

(7) Unbuffered tans can release an appreciable amount of ionizable sulphate, and

apparently this can occur by the liberation of free hydrions, causing greater acidity in the final state of the system.

(3) *The influence of basicity on the stability of the chrome complex*

Experiment 2. With box calf 'L 1' and '4470'.

In view of the experiment of the preceding section being based on a sample showing a minimum content of chromic oxide for a full-chrome tannage, it was deemed desirable to repeat the observations on two other specimens of the same class but having more adequate chrome contents. These two were specially chosen also for their basicities which were equal in amount (9 units) more or less to the basicity of the first leather; the following are their principal features:

%	'L 1'	'613'	'4470'
Moisture	17.40	16.10	16.10
Hide substance	71.35	67.16	70.20
Chromic oxide	4.20	2.67	5.57
Sulphate	3.44	2.00	3.06
Basicity	56.8	65.9	74.0

The two specimens differ therefore from '613' chiefly in chrome content and basicity, and the results with these are given in Table 2.

Table 2

Sample ...	'L 1' basicity 56.8						'4470' basicity 74.0					
	Sulphates lost in percentage of the original											
	With P + T + B			With T + B			With P + T + B			With T + B		
System ...	18	35	100	18	35	100	18	35	100	18	35	100
1. Loss	11.71	25.87	47.10	9.56	14.83	29.65	11.30	19.10	39.80	5.10	8.60	22.58
Initial pH	2.60	2.60	2.60	3.24	3.24	3.24	2.60	2.60	2.60	3.24	3.24	3.24
Final pH	2.72	2.79	2.70	3.24	3.22	2.92	2.74	2.75	2.82	3.11	3.28	3.29
2. Loss	26.30	47.40	63.65	35.45	51.75	57.50	9.15	18.80	57.20	27.95	32.30	57.50
Initial pH	5.30	5.30	5.30	8.75	8.75	8.75	5.57	5.57	5.57	8.88	8.88	8.88
Final pH	5.26	5.14	4.69	8.35	8.17	6.38	5.38	5.25	4.69	8.60	8.40	6.20
3. Loss	50.55	57.80	75.30				42.50	44.75	75.80			
Initial pH	8.70	8.70	8.70				8.68	8.68	8.68			
Final pH	8.15	7.95	6.22				8.76	8.50	6.44			
System no.	Chrome oxide lost in percentage of the original											
1	Traces	Traces	0.18	0.04	0.26	0.38	0.06	—	Nil	0.27	0.45	0.18
2	0.07	0.05	0.38	0.24	0.24	1.67	0.09	0.09	0.23	0.27	0.87	1.00
3	0.24	0.24	0.36				0.09	0.09	1.10			

The following statements on this experiment can be made:

(1) All conclusion of § 1 are valid in this experiment. A linear function of sulphate loss against temperature does not apply to 'L 1' though it does to '4470' below pH 6.0 (see Fig. 1).

(2) The leather with the higher basicity, viz. '4470', is the more resistant to SO₄ and Cr losses under all conditions of temperature and pH irrespective of the presence of perspiration.

(3) The previous deduction does not apply in its entirety as between 'L 1' of Table 2 and '613' of Table 1, and an explanation can be sought in the comparison of the chromium losses which are greater with '613' in spite of the higher basicity. Although the deter-

mination of chromium in small amounts is liable to increased experimental error, the figures leave no doubt that 'L 1' with the lower basicity shows smaller losses, most probably due to its higher original fixed chrome content—as much as 60% more than '613'.

Experiment 3

In order to confirm the explanation just given, a willow-calf sample was chosen which analysis disclosed as containing 4.00% chromic oxide and 63.9% basicity. Thus this sample, S, resembled 'L 1' in respect of chrome content and '613' in respect of basicity. In view of the comparatively strong action of perspiration which might mask any observable differences between S and '613', especially when these are only 2 units apart in basicity, Table 3 was compiled, using the system of buffered tans only.

The data show unmistakably that of the two materials of substantially similar basicity, less sulphate and chromium are lost by the material with higher chrome content, at least up to the temperatures of a warm foot.

Table 3

System ...	Willow calf S: total SO ₄ , 2.74%; Cr ₂ O ₃ , 4.00%; basicity, 63.9.			Box calf '613': total SO ₄ , 2.00%; Cr ₂ O ₃ , 2.67%; basicity, 65.9.		
	With T + B					
Temp. ° C. ...	18	35	100	18	35	100
	Sulphates lost in percentage of original					
1. Loss	8.39	15.00	45.60	16.85	23.40	44.80
Initial pH	3.34	3.34	3.34	3.18	3.18	3.18
Final pH	3.28	3.28	3.06	3.23	3.19	3.04
2. Loss	28.25	42.30	—	36.60	52.00	—
Initial pH	8.65	8.65	—	8.52	8.52	—
Final pH	8.23	8.06	—	8.34	8.12	—
System no.	Chromic oxides lost in percentage of original					
1	0.62	1.25	1.87	0.76	0.76	1.91
2	0.06	0.62	—	0.19	0.38	—

It is likely that something more is involved than mere basicity coupled with chrome content. The precise manner of co-ordination of the ionized radicles to the protein as well as to the chromium must doubtless affect reactivity against buffered tans. In illustration of this possibility, the following experiment is of interest:

Experiment 4

(A) Box calf '613' as extracted with 6% sodium chloride at 35° C. and deprived of 37.5% of its sulphates (see Colin-Russ, 1940, Table 1) was further extracted for another hour at the same temperature. The sulphate loss proved to be 62.5%, thus completely eliminating in this case the sulphate of the tannage.

(B) Box calf '613' was extracted with P and B reagents at 100° C. in the presence of 60 g. solid potassium chloride. Compared with the data already given in the first table under P + B, much less sulphate with chromium was obtained, thus:

	KCl absent	With KCl to saturation
% loss SO ₄	69.95	39.95
% loss Cr ₂ O ₃	3.82	0.38
Initial pH	2.69	2.42
Final pH	3.12	3.12

We may therefore deduce from this experiment, that whilst weak salt solution can displace co-ordinated sulphate as much as 88.9% (see Colin-Russ, 1940, Table 1),

saturation with salt appears to involve the entry of chloride ions into the co-ordination complex in such a way that only 40% of the sulphate can be released from the chrome-protein combination at 100° C.; apparently a new configuration is induced within the complex. As much as 30% of the sulphate is protected from attack by the buffered perspiration.

(4) *The effect of soap solutions on the chrome complex*

In view of the results from the foregoing experiments, it seemed logical to investigate the action of soap solution regarded as a buffer of the alkali-long chain fatty acid type. The accounts which follow show that this work led in turn to indicating how upper leather of basic chrome sulphate tannage might be rendered reasonably 'spue proof'.

Experiment 5

(A) A solution of 5% sodium stearate was prepared, adjusted with a drop or two of acetic acid so as to decolorize phenolphthalein. 100 ml. of this and 5 g. of box calf '613' were heated for 1 hr. The hot supernatant liquid was then decanted and the residual leather well washed. Then 20 ml. *N* HCl were added to the liquid and washings, and after cooling the precipitated fatty acids were filtered, washed, and the final filtrate and washings titrated against *N*/10 NaOH with methyl orange indicator. A back titration was also done on a control test. Each neutralized solution was next concentrated to a bulk of $\frac{1}{4}$ l., filtered after clarification with 'Hyflo', and sulphate determined in the usual way, followed by chrome-oxide evaluation in the filtrate from the barium sulphate, using the fusion method.

(B) This experiment was a repetition of (A) except that 200 ml. of the stearate were used at 2.5% and the temperature was reduced to 55° C. Maximum concentration was secured in this way at minimum temperature for liquefaction of the soapy phase. In this case it was necessary to allow complete melting of the fatty acids to an agglomerate before cooling, filtering and washing.

(C) This experiment was a repetition of B except that a single cutting of the leather was used, instead of pieces $\frac{1}{2}$ cm. sq.

(D) This experiment represented one of the trials done at room temperature and for it sodium palmitate was found to be more suitable in keeping liquid even at 1% concentration. 200 ml. of 1% solution and 5 g. pieces of the box calf were allowed to stand at 15° C. for 65 hr. before analysis.

The data are given in Table 4:

Table 4. *Box calf* '613'

Exp. no.	Sulphates lost		Chromic oxide lost		Titration difference <i>N</i> /10 ml.
	g. SO ₄ corr.	% of total	g. Cr ₂ O ₃	% of total	
5 A	1.09	54.5	0.030	1.12	24.0
5 B	1.44	72.0	0.025	0.95	23.0
5 C	1.85	92.5	0.020	0.74	25.0
5 D	0.04	2.0	0.020	0.74	17.5

Blank for SO₄ from sodium stearate, 0.04%; for Cr₂O₃, nil

Evidently the soap treatment extracts more sulphate when the ratio of liquid to leather is increased and is better still when the leather is kept uncut. For this particular leather,

the shrinkage was not good originally, being 44.6%, and after treatment with soap increased to 57.6%.

It was instructive to test the treated cutting by boiling for 1 hr. with 10% synthetic perspiration. It was found that 0.24% SO_4 and 0.028% chromic oxide were obtained. Since the original total SO_4 was 2.00% and Exp. 5 C showed that 1.85% had been extracted, the value now found of 0.24% means that all the remaining sulphate was eliminated. Where the test yielded a 54.6% loss of the original total in the untreated leather, it now yielded only 12% extractable from the treated state. This can only mean the prospect of a considerable diminution in the formation of Glauber's salts by the action of perspiration on the upper leather, a point in favour of the treatment even though the shrinkage test is unfavourable.

Experiment 6

In order to check Exp. 5 C on a more practical scale, a cutting 10 in. sq. and weighing 54 g. (about 2 oz.) was immersed for 3 hr. at 55° C. in 2 l. of 2.5% soap flakes, 'Sylvan' brand. On removal, rinsing and drying carefully, the dimensions were only reduced to 9.9 in. sq. The shrinkage was therefore only 2%. Furthermore, on testing as before with boiling 10% synthetic perspiration, 0.66% SO_4 was detected instead of 1.09%.

Subsequent experiments revealed that a double treatment was necessary, making the second treatment with fresh soap solution, in order to secure sufficient reduction in the sulphate precipitable by boiling perspiration reagent.

Experiment 7

This one example is chosen out of many to illustrate the foregoing with a willow skin weighing over 1 lb. (464 g.). This willow calf, '629', did not shrink in area when tested for adequate tannage; it had 4.23% chromic oxide, 67.95% hide substance, basicity 52.9 and total SO_4 3.78%.

After the first treatment, 0.62% SO_4 were extractable, reducing to 0.16% after a second treatment. The skin retained after the second treatment 3.92% Cr_2O_3 and 0.66% SO_4 or only 17% of the original sulphate. Thus, whilst the treatment eliminated 83% of the sulphate from the tannage and raised the basicity to 91, boiling perspiration reagent could extract only 4%. If a reduction in the incidence of Glauber's salts deposition in the vamps could be effected down to 4% of the present frequency, it would be of benefit to producers and wearers alike.

This experimental section therefore leads to the following recommendation for lessening spue risks with upper leather. Immerse the skin in 40 times its weight of 2.5% soap solution for 3-4 hr. at 55° C. Flakes are preferred because of their purity, but hard yellow soap can be used and the pH should always be adjusted to about 8.3, viz. when phenolphthalein is only just coloured red by the solution. Usually, a few drops of acetic acid are required to neutralize free alkalinity. Repeat the immersion in a similar way with fresh soap solution, then rinse well and leave to air-dry out thoroughly. The used soap can be recovered by evaporation but it is not then good enough for the purpose of replacing sulphate of chrome tannages. The method is expensive unless the soap can be recovered and utilized, say for the making of fat-liquor emulsions.

(5) *Brown grain chrome uppers as a special class*

Glauber's salts have been frequently observed as spues on brown grain chrome uppers. The heavier quality and special construction of shoes made with this leather, particularly when soled with rubber composition material, often promotes undue warmth of the foot. One example will suffice: basicity 50.4, Cr₂O₃ 3.33%, total SO₄ 3.14% and hide substance 70.0%.

Experiment 8

The data are given in Table 5 restricted to one temperature—that of the warm foot.

(1) The results show an unusually firm tenacity of the chromium when the comparison is made with results from Tables 1 and 2.

(2) A somewhat smaller loss of sulphate than the three leathers of Tables 1 and 2; this means that the performance of brown grain, despite a basicity of 50, may equal in the conditions of the testing system chosen that of a higher basicity, well-chromed box calf.

Table 5

System ...	P + T + B at 35° C.			Final pH
	Loss in percentage of original			
Initial pH	SO ₄	Cr ₂ O ₃		
2.83	15.6	Trace		2.96
6.02	31.2	0.01		5.86
9.79	45.8	0.01		8.35
System ...	T only, at 35° C.			
3.33	5.1	Trace		3.96

(3) As perspiration takes on a lesser degree of acidity, the percentage of the sulphate in the tannage which is converted into Glauber's salts by perspiration, increases from 15% to over 30% in the true neutrality region and finally to over 45% when definitely alkaline. Washed-out tans from insoles normally exercise only a small similarly adverse effect but contribute appreciably to the total perspiration effect within the shoe.

(6) *Foot-bath experiments**Experiment 9*

About 2 gal. of brine (27.4% w/v) were prepared and a volunteer's normal foot dipped into it. The subsequent procedure is shown in the following descriptive data:

Volume of brine in which foot is to be dipped bare up to the calf-muscle	8.80 l.
Increase of volume on dipping	1.95 l.
Analysis of 1st rinse for quantity of salt left on foot after one dip and wipe with towel	0.25 g.
Analysis of 2nd rinse for quantity of salt left on foot after repeating both immersion and wiping 10 times	0.20 g.

These results show that successive dips do not necessarily involve cumulative amounts of salt on the skin. Further examination showed the absence of any serious risk of moisture carrying salts down the leg towards the shoe interior. More likely, the hose would absorb such moisture.

As regards the length of the foot portion that would be inside a shoe it measured 28 cm., and in view of the length corresponding to one dip being 43 cm. the proportionate amount of salt that might be washed through the shoe vamps by perspiration would be 28/43rds of 0.25 g. or 0.16 g.

Now if the foot bath is of sea water or of a solution of 'Radox', 'Reudel', or other

well-known proprietary product, all of which contain generally 2-3% salt, then this forms 1/10th the strength of the above experimental case.

Thus perspiration would wash out 0.016 g. salts after every foot bath. It is estimated that such a foot bath would have to be done every alternate day for 8 days before any decomposition of the upper leather could be observed to the extent given in Tables 1 and 2. That cumulative traces, if any, of salts from foot baths can cause disruption of the upper leather fibres with foot perspiration functioning merely as an aqueous solvent is unlikely. The constituents of perspiration remain the most fundamental cause.

(7) *Cause of darkened and cracked grain surface of worn insoles*

In view of the usual association of insole tans with perspiration when the latter works its way through the shoe uppers, it is fitting to conclude this experimental part of the paper with an account of a small investigation into darkened and cracked insoles of bark tannage.

Experiment 10

Grain-skivings of the dark cracked parts and the whole substance of the comparatively unaffected parts near the 'waist' (flesh cleaned) were separately analysed as given in Table 6.

Table 6

	Dark grain skivings %	Unaffected parts %
Fat	0.33	1.34
Water solubles	8.50	13.90
pH	6.28	4.48
Colour	Dark	Pale tan
Ashed insolubles	1.37	0.16
Hide substance	48.90	43.00
Fixed tan by difference*	26.90	27.60
	<u>100.0</u>	<u>100.0</u>
Degree of tannage	55.00	64.15
Collagen tannate	75.80	70.60
Total ash	2.27	1.06
Water-soluble nitrogen calculated as hide substance:		
Total	1.18	1.34
Free ammonia	0.79	0.95

* Assuming 14% moisture.

The following comments may be made:

(1) The dark appearance persists in the aqueous extract and this is due to mild alkaline influence, judging by the higher pH.

(2) The higher pH in turn is associated with a higher concentration of nitrogenous matter, part of which may be released as free ammonia; in order to elicit the relative concentrations, the N content is calculated as equivalent hide substance:

	Dark parts	Unaffected parts
% total N in water solubles	13.9	9.6
% free N in water solubles	9.3	6.85

(3) There is a loss of grease content during wear.

(4) There is a loss of water solubles during wear, and the decrease is actually greater than that observed, namely 5.4% difference value or 38.85% of the original content,

because the latter exists in the *whole* substance whereas the dark parts always show on analysis the larger fraction of the total solubles.

(5) There is a loss of fixed tan, the exact extent of which was not ascertainable, owing to paucity of material which made it impossible to evaluate the moisture item reliably.

(6) Hydroxy-acids and chlorides from perspiration were found in the dark parts, *not* in the unaffected; doubtless, the higher ash content may be due to this.

It would appear that some wearers possess a higher rate of nitrogenous metabolism as manifested by cumulative action of the urea or uric acid type of perspiration. The present studies will therefore continue with this aspect particularly in mind.

SUMMARY

IN CONTINUATION OF PREVIOUS WORK INVOLVING ACCENTUATED EFFECTS OF PERSPIRATION ON CHROME UPPER LEATHER, THE PRESENT PAPER RECORDS OBSERVATIONS OF SUCH EFFECTS IN MORE COMPLICATED CONDITIONS.

Thus, effects were studied at varying temperatures and pH of tans, buffered tans, buffered perspiration, buffered perspiration coupled with tans, buffering material itself and soap solutions.

Particular reference is made to the influence of basicity on the stability of the chrome complex against perspiration in such buffered chemical systems. Brown grain leathers are considered as well as box and willow calf.

A method is evolved for minimizing spueing risks or the formation of Glauber's salts in the vamps of worn footwear, by appropriate treatment of the skins before cutting up into shoe upper components.

Finally, some foot-bath experiments and the dark, cracky grain of worn insoles are discussed from the general point of view of perspiratory action on footwear.

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