



| | |
|------------------|--|
| Title | Composition of Complexes in Chrome Tanning Liquors and Its Effect on Heat Resistance |
| Author(s) | TAKENOUCHI, Kazuaki |
| Citation | Journal of the Faculty of Agriculture, Hokkaido University, 60(3), 194-219 |
| Issue Date | 1981-09 |
| Doc URL | http://hdl.handle.net/2115/12957 |
| Type | bulletin (article) |
| File Information | 60(3)_p194-219.pdf |



[Instructions for use](#)

COMPOSITION OF COMPLEXES IN CHROME TANNING LIQUORS AND ITS EFFECT ON HEAT RESISTANCE

Kazuaki TAKENOUCHI

Department of Animal Science, Faculty of Agriculture,
Hokkaido University, Sapporo, 060, Japan

Received April 30, 1981

Introduction

Chrome tanning liquors contain a wide variety of chromium complexes of different structures. The composition of the complexes causes a marked change in the tanning properties of the liquors and in the qualities of leathers produced.

In practical chrome tanning, chromium sulfate is usually used as the fundamental tanning material, while chromium chloride or perchlorate is seldom used. It is well known that glucose-reduced chrome tanning liquors produce leathers with better qualities than inorganically reduced chrome liquors.

Basic chromium chloride solutions contain a large quantity of olated complexes, polymerized complexes. The olated complexes fix on the outside of hide, preventing the penetration and leaving the interior of the hide in an untanned or undertanned state. Sulfate and carboxylate groups present in chromium sulfate or glucose-reduced chrome solutions coordinate with chromium atoms and result in a mild and slow tanning action, improving the penetration and resulting in uniform chrome distribution within the leathers.

Recently, several complexes present in chrome tanning liquors were separated by ion-exchange chromatography and characterized by their visible absorption spectra, charge, and ratios of ligand to chrome^{1,2,3}. But unfortunately, the complexes are so easily changed by surrounding factors that the reactivity pattern of these individual complexes with hide substance has not yet been assessed completely.

In this paper, the composition of complexes in three kinds of chrome

* Presented at the 181st American Chemical Society national meeting, Atlanta, Georgia, U.S.A., April 3, 1981.

[J. Fac. Agr. Hokkaido Univ., Vol. 60, Pt. 3, 1981]

solutions, chromium chloride, chromium sulfate, and glucose-reduced chrome solutions, was studied first. Second, the affinity of the individual complexes with hide substance was studied. Third, the denaturation of tanned hide substance through heating was discussed in relation to the kind of the complexes.

Experimental

Materials

Three kinds of chrome solutions, chromium chloride, chromium sulfate, and glucose-reduced chromium sulfate, were prepared as typical tanning liquors.

The chromium chloride and chromium sulfate solutions were prepared by dissolving chromium chloride, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, and chromium sulfate, $\text{Cr}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$, respectively. The glucose-reduced chromium sulfate solution was prepared from sodium bichromate by reduction with glucose. The reduction was carried out by adding 36.8 g of sulfuric acid to a boiling mixture of 37.3 g of bichromate and 8.44 g of glucose⁹. The amounts of sulfuric acid and glucose were equivalent to theoretical 33 percent basicity and 150 percent of the theoretical amount required, respectively.

All the solutions were adjusted to 33 percent basicity by adding sodium hydroxide, diluted to 0.1 M Cr, and aged for about one month at room temperature. pH of all the solutions was around 3.

Hide powder was prepared from the middle layer of delimed hide.

Complex Separation and Characterization

Gel filtration was carried out with Sephadex G 25 (90×2.6 cm). Test samples (5 ml) were applied to the column and then eluted by 0.1 M NaCl. The rate of flow was 50 ml/hr. The effluent was collected as 5 ml fractions with a fraction collector and monitored at 420 nm using a spectrophotometer.

Ion-exchange was carried out with SP-Sephadex C 25 (20×1.6 cm), swollen in 0.2 M NaCl. Test samples (10 ml) were applied to the column and then eluted by gradient elution with sodium chloride. The starting buffer was 100 or 150 ml of water and the limit one was 3 M NaCl. The gradient formed was convex and exponential. The rate of flow was 30 ml/hr. The effluent was collected as 4 ml fractions and monitored at 420 nm.

The visible absorption spectra of separated complexes were measured with a Shimadzu UV-210 A spectrophotometer.

The infrared absorption spectra of separated complexes were measured in potassium bromide disks with a Shimadzu IR-400 infrared spectrophoto-

meter after desalting and freeze drying⁵¹.

Tanning Methods

Hide powder (1.0 g) was soaked in $\text{NaClO}_4\text{-HClO}_4$ mixture (10 ml) for 2 hr to get the desired tanning pH values and tanned for 22 hr at 30°C with chrome solutions (20 ml). No extrenal pH alteration was made. pH tended to decrease somewhat during tannage.

Analysis of Hide Powder and Tanning Effluents

Chromium fixed on hide powder was determined by the fusion method with sodium peroxide. Collagen was determined by the Kjeldahl method. The chrome content was calculated as percent Cr_2O_3 on the collagen.

The effluents and washings after tanning were collected quantitatively. The amounts of various complexes and their distribution in the effluent were estimated after Sephadex separation.

Estimation of Heat Resistance

The heat resistance of tanned hide powders was estimated by solubility, infrared spectra, and differential thermal analysis (DTA) curves.

Tanned hide powders (100 mg) which passed 35 mesh sieve were heated in water (20 ml) at 75°C for 24 or 48 hr or in air at 180°C for six days. The heated powders were extracted with 500 ml of water by using a fritted glassware (20~30 μm opening). The absorption of the extracts were measured at 194 nm. Insoluble materials were dried at 100°C overnight. Solubility was calculated as percent on dry material.

Tanned hide powders which were homogenized with a Polytron homogenizer and then freeze-dried were heated at 180°C for ten days. The heated powders were ground in a mortar, mixed with potassium bromide, and pressed. The absorption of the pellets obtained was measured with a Shimadzu IR 400 infrared spectrophotometer.

Tanned hide powders (about 5 mg) which passed 35 mesh sieve were put in aluminium pans and then sealed in order to prevent the evaporation of water. The test samples and the reference ($\alpha\text{-Al}_2\text{O}_3$) were put in holders of a Rigaku TG-DTA apparatus. The samples were heated at 5°C per minute. The sensitivities used were ± 25 and $\pm 10 \mu\text{v}$. Since thermal stability of leathers varied with their water contents⁶¹, DTA was done with tanned hide powders of different water contents. The powders were left in room and in a desiccator with water, of which water contents were 12 and 40 percent, respectively.

Results and Discussion

Composition of Complexes

(a) 33 Percent Basic Chromium Chloride

33 percent basic chromium chloride was gel-filtrated. The elution pattern of Fig. 1 shows the chrome solution separated into two major components, with indications of a minor component which elutes before the two major components. In this paper, the components separated by gel filtration chromatography will be termed components A, B, C ... in order of their elution. Components A and B were green and component C was violet.

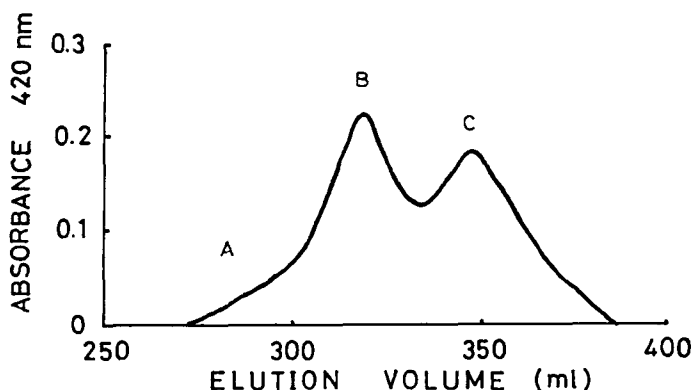


Fig. 1. Gel filtration chromatogram of 33 percent basic chromium chloride on Sephadex G 25 (90×2.6 cm) eluted with 0.1 M NaCl, 5 ml fractions.

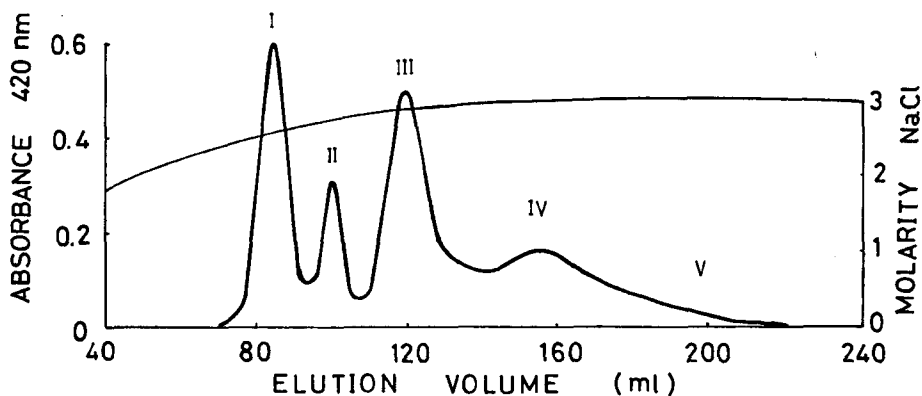


Fig. 2. Ion-exchange chromatogram of 33 percent basic chromium chloride on SP-Sephadex (20×1.6 cm) eluted with 3 M NaCl, 4 ml fractions.

Earlier eluted components are larger-sized complexes in gel filtration chromatography. Hexaaquochromium complexes eluted at the same region as Component C. Therefore, Components A, B, and C are considered to be large-, medium- and small-sized complexes, respectively. From Fig. 1 it is suggested that 33 percent basic chromium chloride contains a small quantity of large-sized complexes in addition to large quantities of medium- and small-sized complexes.

33 percent basic chromium chloride was ion-exchanged. The ion-exchange chromatogram of Fig. 2 shows the chrome solution separated into five components, of which two components were major ones. A very small quantity of complexes did not elute and stayed in a column. In this paper, the components separated by ion-exchange chromatography will be termed components I, II, III, ... in order of their elution. Although component I was violet, its leading edge was green. Component II was bluish-green and the others were green.

Earlier eluted components are lower-charged complexes in ion-exchange chromatography. Hexaaquochromium complexes eluted at the same region as component I. Therefore, components I to IV correspond to $+3$ to $+6$ charged complexes, respectively. A trailing component, component V, and a component staying in a column, component VI, may be the complexes having very high charges.

From Fig. 2 it is suggested that most of complexes present in 33 percent basic chromium chloride have considerable charges corresponding to $+3$ to $+6$.

In order to make sure of the relation between size of complexes and charge of ones, two major components separated by gel filtration chromatography were ion-exchanged. The elution patterns obtained are shown in Fig. 3. Component B was composed of a large quantity of component III and a small quantity of component IV, while component C was composed of a large quantity of component I, a considerable quantity of component II, and a small quantity of component III.

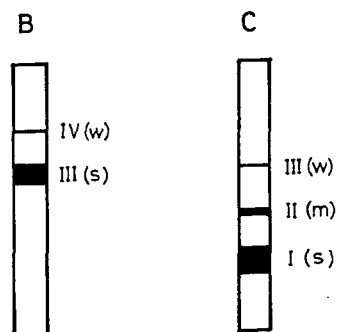
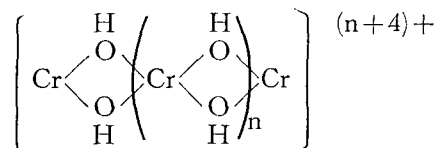


Fig. 3. Ion-exchange chromatograms of components from gel filtration of 33 percent basic chromium chloride on SP-Sephadex eluted by gradient elution with 3 M NaCl. (w=weak; m=medium; s=strong)

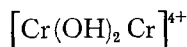
From the results obtained, it is suggested that larger-sized complexes are higher-charged complexes. Components I and II may be small-sized complexes and components III and IV may be medium-sized complexes. Components V and VI are considered to correspond to component A, large-sized complexes.

The formation of polynuclear complexes by the addition of alkali may take place in such manner that two hydroxo groups are held in the enlarged nucleus by two chromium atoms, as follows⁹:

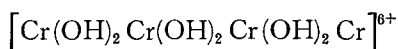
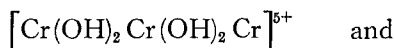


Component I which is violet is obviously hexaaquochromium complexes. Because almost all the complexes present in a hexaaquochromium chloride solution corresponded to component I.

Since component II corresponds to small-sized and +4 charged complexes, their structure may be represented as follows:



Components III and IV correspond to medium sized complexes and to +5 and +6 charged complexes respectively. These complexes may be represented as follows:



Components V and VI must be larger-sized and higher-charged complexes than the complexes described above.

The composition of complexes in 33 percent basic chromium chloride is shown in Table 1. The largest quantity was hexaaquo complexes, and the complexes corresponding to tetra- μ -hydroxo trichromium complexes were next in order of quantities.

The visible absorption spectral characteristics of each component are shown in Table 2. All components showed maximum absorption in two regions, roughly around 420 and 580 nm. The wave lengths of peaks of components II, III, and IV were longer than that of component I and their molar extinction coefficients (E) were much higher. E values of components

TABLE 1. Composition of complexes in 33% basic chromium chloride

| Component | Formula | Distribution (%) |
|-----------|---|------------------|
| I | [Cr] ³⁺ | 37 |
| II | [Cr(OH) ₂ Cr] ⁴⁺ | 13 |
| III | [Cr(OH) ₂ Cr(OH) ₂ Cr] ⁺⁵ | 29 |
| IV | [Cr(OH) ₂ Cr(OH) ₂ Cr(OH) ₂ Cr ⁶⁺ } | 20 |
| V | [Cr(OH) ₂ Cr.....Cr] ⁿ⁺ | |
| VI } | | |
| | | 1 |

III and IV were higher at the first peak than at the second peak. As the results, their ratios of the molar extinction coefficients, E_1/E_2 , were high.

As described above, component I is hexaquo complexes and the other components are polymerized complexes. It is seen from Table 2 that the polymerization results in both a shift of peaks to longer wave lengths and an increased molar extinction coefficient, particularly at the first peak. This is in agreement with LASWICK and PLANE's view⁷.

TABLE 2. Visible spectral characteristics of components from 33% basic chromium chloride

| Component | Color | 1st Peak | | 2nd Peak | | $R = E_1/E_2$ |
|-----------|--------------|----------|---------|----------|---------|---------------|
| | | nm | E_1^* | nm | E_2^* | |
| I | Violet | 409 | 15.6 | 576 | 13.6 | 1.15 |
| II | Bluish-green | 417 | 21.6 | 583 | 18.5 | 1.17 |
| III | Green | 423 | 29.1 | 584 | 19.4 | 1.50 |
| IV | Green | 423 | 31.4 | 585 | 20.3 | 1.55 |
| V, VI | Green | — | — | — | — | — |

* E: Molar extinction coefficient

(b) 33 Percent Basic Chromium Sulfate

The gel filtration chromatogram of 33 percent basic chromium sulfate is shown in Fig. 4, which shows a separation into two major components. Although these components were bluish-green, the earlier eluted part of component A was green. The total volume of elution was smaller than that of 33 percent basic chromium chloride. This is due to the disappearance of the much earlier eluted components, indicating the absence of large-sized complexes.

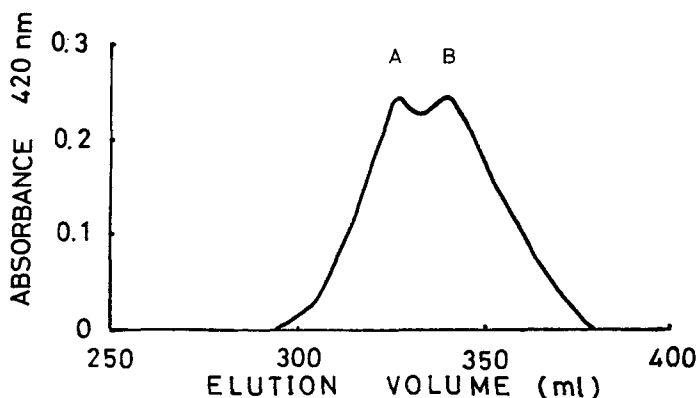


Fig. 4. Gel filtration chromatogram of 33 percent basic chromium sulfate on Sephadex G 25 (90×2.6 cm) eluted with 0.1 M NaCl, 5 ml fractions.

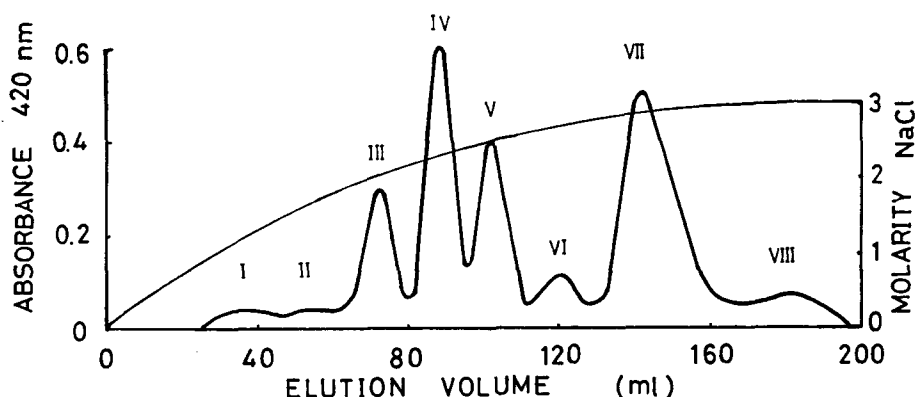


Fig. 5. Ion-exchange chromatogram of 33 percent basic chromium sulfate on SP-Sephadex (20×1.6 cm) eluted with 3 M NaCl, 4 ml fractions.

From Figure 4 it is suggested that 33 percent basic chromium sulfate is composed of small- and medium-sized complexes.

The ion-exchange chromatogram of 33 percent basic chromium sulfate is shown in Figure 5, which shows a separation into eight components. Of these, components III, IV, V, and VII were major components. Components I to IV were bluish-green, component V was violet, and components VI to VIII were green.

The electric charges of chromium complexes present in each component were inferred from their elution regions compared with those of dioxalato-diaquochromate and hexaquo-chromium complexes, -1 and $+3$ respectively.

Components I and II correspond to anionic and nonionic complexes, respectively. Components III to VIII correspond to +1 to +6 charged complexes, respectively.

From Fig. 5 it is suggested that 33 percent basic chromium sulfate contains large quantities of lower-charged complexes in addition to a large quantity of the complexes with charge corresponding to +5.

The ion-exchange chromatograms of components A and B from gel filtration of the basic chromium sulfate are shown in Fig. 6. Components A and B were enriched in components VII and IV, respectively. Component V was present in both components A and B.

From the results described above, it is presumed that component VII is medium-sized complexes and that components III, IV, and V are small-sized complexes.

The visible absorption spectral characteristics of each component from ion-exchange are shown in Table 3. The characteristics of component V were much similar to those of hexaaquo complexes. The others were longer

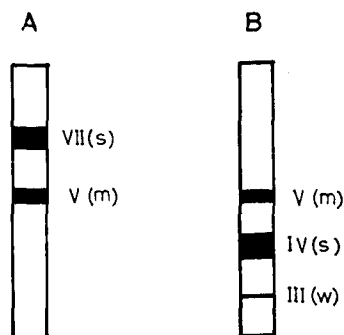


Fig. 6. Ion-exchange chromatograms of components from gel filtration of 33 percent basic chromium sulfate on SP-Sephadex eluted by gradient elution with 3 M NaCl. (w=weak; m=medium; s=strong)

TABLE 3. Visible spectral characteristics of components from 33% basic chromium sulfate

| Component | Color | 1st Peak | | 2nd Peak | | $R = E_1/E_2$ |
|-----------|--------------|----------|---------|----------|---------|---------------|
| | | nm | E_1^* | nm | E_2^* | |
| I | Bluish-green | 425 | 24.3 | 593 | 26.3 | 0.92 |
| II | Bluish-green | 421 | 21.3 | 592 | 22.9 | 0.93 |
| III | Bluish-green | 419 | 19.8 | 585 | 19.9 | 0.99 |
| IV | Bluish-green | 418 | 17.7 | 582 | 16.7 | 1.06 |
| V | Violet | 410 | 16.7 | 576 | 14.8 | 1.13 |
| VI | Green | 419 | 21.3 | 586 | 16.7 | 1.28 |
| VII | Green | 424 | 29.3 | 584 | 19.2 | 1.53 |
| VIII | Green | — | — | — | — | — |

* E : Molar extinction coefficient.

in wave length at both peaks and higher in molar extinction coefficient than component V. Components I, II, III, and IV were lower in E_1/E_2 than component V, while components VI and VII were higher. The characteristics of components VI and VII were much similar to components II and III of 33 percent basic chromium chloride. The characteristics of components I to IV may be due to the coordination of sulfate groups.

This view was supported by infrared spectra of each components shown in Fig. 7. Components I to IV showed bands indicative of sulfato groups in the 900 to 1300 cm^{-1} region^{5,9}. The band at 1200 cm^{-1} of component IV suggests that the sulfato groups coordinate as bidentates. The weak band at 1600 cm^{-1} is indicative of water. Component V showed very weak bands indicative of sulfato groups, indicating the presence of a very small quantity of sulfato complexes. Most of component V may be hexaaquo complexes. Components VI to VIII showed only the band indicative of

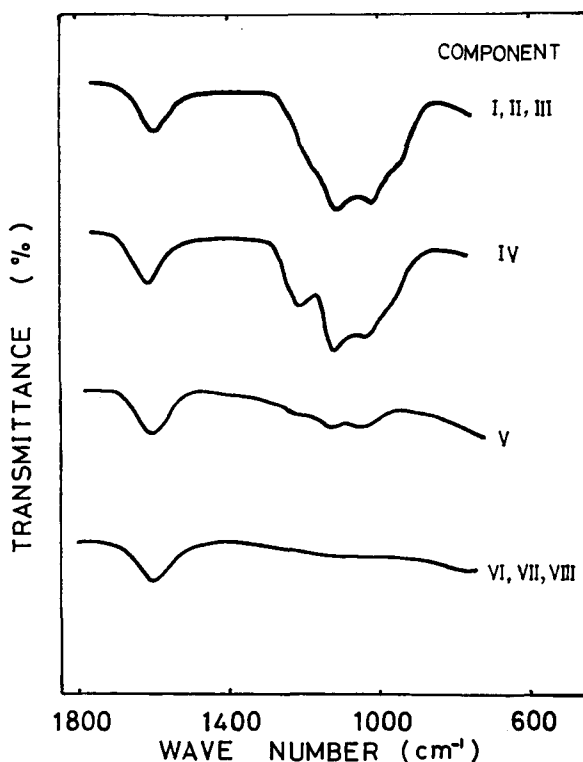


Fig. 7. Infrared spectra of components from 33 percent basic chromium sulfate.

water at 1600 cm^{-1} , suggesting that these components are hydroxo complexes.

The characteristics of both the visible and infrared absorption spectra described above support the structural elucidation reported in a previous paper from this laboratory⁹. Complexes present in each component may be represented as follows (omitting H_2O):

Component

| | |
|------|--|
| I | $[\text{Cr}(\text{SO}_4)_2]^-$ |
| II | $[\text{Cr OH SO}_4]$ |
| III | $[\text{Cr SO}_4]^+$ |
| IV | $[\text{Cr}(\text{OH})_2\text{SO}_4 \text{ Cr}]^{2+}$ |
| V | $[\text{Cr}]^{3+}$ |
| VI | $[\text{Cr}(\text{OH})_2 \text{ Cr}]^{4+}$ |
| VII | $[\text{Cr}(\text{OH})_2 \text{ Cr}(\text{OH})_2 \text{ Cr}]^{5+}$ |
| VIII | $[\text{Cr}(\text{OH})_2 \text{ Cr}(\text{OH})_2 \text{ Cr}(\text{OH})_2 \text{ Cr}]^{6+}$ |

These structure are essentially in agreement with those shown by SLABBERT, KÜNTZEL and MAHDI^{1,9}.

The composition of complexes present in 33 percent basic chromium sulfate is shown in Table 4. Main complexes were the complexes corresponding to di- μ -hydroxo- μ -sulfato dichromium, hexaaquochromium, and tetra- μ -hydroxo trichromium complexes.

TABLE 4. Composition of complexes in 33% basic chromium sulfate

| Component | Formula | Distribution (%) |
|-----------|--|------------------|
| I | $[\text{Cr}(\text{SO}_4)_2]^-$ | } 3 |
| II | $[\text{CrOHSO}_4]$ | |
| III | $[\text{CrSO}_4]^+$ | |
| IV | $[\text{Cr}(\text{OH})_2 \text{ SO}_4\text{Cr}]^{2+}$ | 25 |
| V | $[\text{Cr}]^{3+}$ | 22 |
| VI | $[\text{Cr}(\text{OH})_2 \text{ Cr}]^{4+}$ | 5 |
| VII | $[\text{Cr}(\text{OH})_2 \text{ Cr}(\text{OH})_2 \text{ Cr}]^{5+}$ | 24 |
| VIII | $[\text{Cr}(\text{OH})_2 \text{ Cr}(\text{OH})_2 \text{ Cr}(\text{OH})_2 \text{ Cr}]^{6+}$ | 8 |

(c) 33 Percent Basic Glucose-Reduced Chromium Sulfate

The gel filtration chromatogram of Fig. 8 shows 33 percent basic glucose-reduced chromium sulfate separated into three components, bluish-

green, bluish-green, and reddish-violet components in order of elution. The earlier eluted part of component A was green. The total volume of elution was small in quantity like that of basic chromium sulfate, indicating the absence of large-sized complexes.

Therefore, it is suggested that 33 percent basic glucose-reduced chromium sulfate is composed of small- and medium-sized complexes.

The ion-exchange chromatogram of Fig. 9 shows 33 percent basic

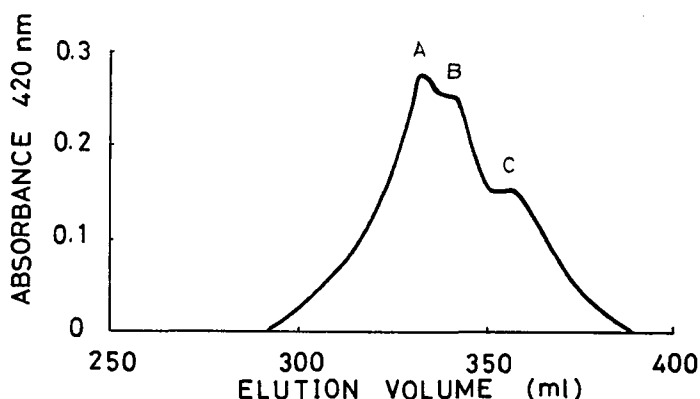


Fig. 8. Gel filtration chromatogram of 33 percent basic glucose-reduced chromium sulfate on Sephadex G 25 (90×2.6 cm) eluted with 0.1 M NaCl, 5 ml fractions.

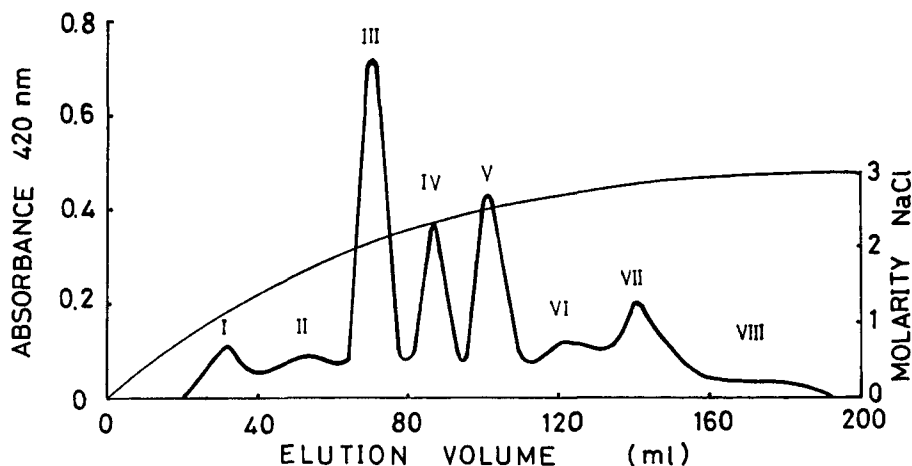


Fig. 9. Ion-exchange chromatogram of 33 percent basic glucose-reduced chromium sulfate on SP-Sephadex (20×1.6 cm) eluted with 3 M NaCl, 4 ml fractions.

glucose-reduced chromium sulfate separated into eight components. Of these, only component III consisted of two subcomponents, a bluish-green one (component III A) and a reddish-violet one (component III B) in order of elution. Components III, IV, and V were major components.

From the elution regions of each component, it is inferred that components I and II are anionic and nonionic complexes, respectively and that components III to VIII are +1 to +6 charged complexes, respectively. Therefore, it is suggested that 33 percent basic glucose-reduced chromium sulfate is chiefly composed of lower-charged complexes corresponding to +1 to +3 charged ones.

The ion-exchange chromatograms of components A, B, and C from gel filtration are shown in Fig. 10. Component A was composed of components V and VII in about equal amounts, while component B was composed of components III A, IV, and V in about equal amounts. Component C was enriched in component III B.

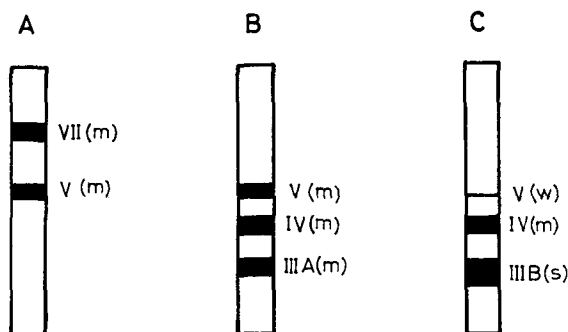


Fig. 10. Ion-exchange chromatograms of components from gel filtration of 33 percent basic glucose-reduced chromium sulfate on SP-Sephadex eluted by gradient elution with 3 M NaCl. (w=weak; m=medium; s=strong)

From the results obtained, it is suggested that component VII is medium-sized complexes and that components III A, III B, IV, and V are small-sized complexes.

The visible absorption spectral characteristics of each component from ion-exchange are shown in Table 5. Component III B showed very high E values at both peaks and short wave length of the second peak. Although component V was violet and eluted in the same region as hexaaquochromium complexes, its characteristics were quite different from those of the hexaaquo complexes. The other components did not show quite different characteristics from those of the corresponding components from basic chromium

TABLE 5. Visible Spectral Characteristics of components from 33% basic glucose-reduced chromium sulfate

| Component | Color | 1st Peak | | 2nd Peak | | R = E ₁ /E ₂ |
|-----------|----------------|----------|-----------------------------|----------|-----------------------------|------------------------------------|
| | | nm | E ₁ [*] | nm | E ₂ [*] | |
| I | Bluish-green | 418 | 29.0 | 577 | 26.7 | 1.09 |
| II | Bluish-green | 420 | 20.9 | 581 | 21.4 | 0.98 |
| III A | Bluish-green | 418 | 20.2 | 581 | 20.3 | 1.00 |
| III B | Reddish-violet | 418 | 38.7 | 559 | 33.2 | 1.17 |
| IV | Bluish-green | 417 | 19.2 | 580 | 18.2 | 1.05 |
| V | Violet | 412 | 19.1 | 576 | 18.5 | 1.03 |
| VI | Green | 418 | 26.1 | 586 | 21.1 | 1.24 |
| VII | Green | 423 | 29.0 | 585 | 19.3 | 1.50 |
| VIII | Green | — | — | — | — | — |

* E: Molar extinction coefficient.

sulfate.

From the characteristics described above, it is suggested that component III B is the complexes which contain such ligands as polycarboxylate ions and that component V is the complexes which contain such ligands as monocarboxylate ions^{10,11}. A bit difference in the characteristics of the corresponding components of basic glucose-reduced chromium sulfate and basic chromium sulfate may be due to a mixture of organo complexes.

The infrared spectra of each component are shown in Fig. 11. Components I and II showed the strong bands indicative of sulfato groups. Component III A showed the weak bands indicative of formato groups in addition to the strong bands indicative of sulfato groups⁹. Component III B showed only the bands indicative of oxalato groups^{5,12}. Component IV showed the strong bands indicative of sulfato and formato groups. Components VI, VII, and VIII showed only the band indicative of water.

From the results described above it is suggested that components I and II are sulfato complexes and that component III B is oxalato complexes. Component III A is considered to be a mixture of sulfato and formato complexes. Component IV also is considered to be a mixture of sulfato and formato complexes or sulfatoformato complexes. Component V may be a mixture of hexaaquo and formato complexes. Components VI to VIII may be hydroxo complexes.

From gel filtration it is suggested that components I to V are mono- or binuclear complexes. It is, therefore, considered that the theoretical

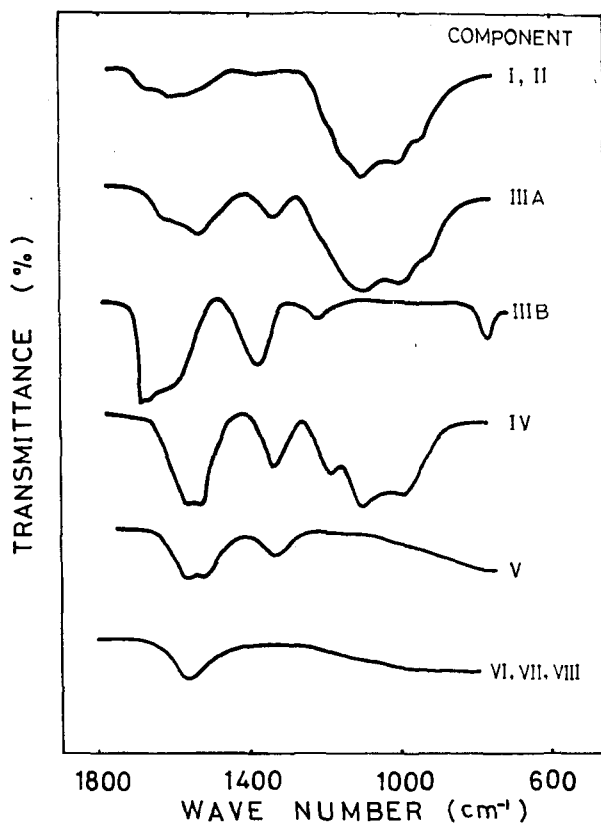
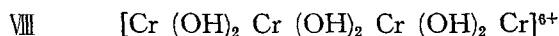
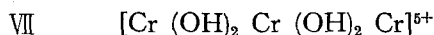


Fig. 11. Infrared spectra of components from 33 percent glucose-reduced chromium sulfate.

ratios of acid to a chromium atom are n or $n/2$ (where n is an integer). The structure of each component may be represented as follows (omitting H_2O)⁹:

Component

| | |
|-------|---|
| I | $[Cr (SO_4)_2]^-$ |
| II | $[Cr OH SO_4]$ |
| III A | $[Cr SO_4]^+ [Cr (fo)_2]^+$ |
| III B | $[Cr ox]^+$ |
| IV | $[Cr OH SO_4 fo Cr]^{2+} [Cr (OH)_2 SO_4 Cr]^{2+} [Cr fo]^{2+}$ |
| V | $[Cr (OH)_2 fo Cr]^{3+}$ or $[Cr OH (fo)_2 Cr]^{3+} [Cr]^{3+}$ |
| VI | $[Cr (OH)_2 Cr]^{4+}$ |



The composition of complexes present in 33 percent basic glucose-reduced chromium sulfate is shown in Table 6. The largest quantity was component V, a mixture of hexaaquo and formato complexes, and component IV, a mixture of sulfato and formato complexes or sulfatoformato ones, was next in order of quantities.

TABLE 6. Composition of complexes in 33% basic glucose-reduced chromium sulfate

| Component | Formula | Distribution (%) |
|-----------|---|------------------|
| I II | $[\text{Cr}(\text{SO}_4)_2]^- [\text{CrOH}\text{SO}_4]$ | 9 |
| IIIA | $[\text{CrSO}_4]^+$ | 10 |
| IIIB | $[\text{Cr ox}]^+$ | 11 |
| IV | $[\text{CrOH}\text{SO}_4 \text{ fo Cr}]^{2+} [\text{Cr}(\text{OH})_2 \text{SO}_4 \text{Cr}]^{2+} [\text{Cr fo}]^{2+}$ | 17 |
| V | $[\text{Cr}(\text{OH})_2 \text{fo Cr}]^{3+}$ or $[\text{CrOH}(\text{fo})_2 \text{Cr}]^{3+} [\text{Cr}]^{3+}$ | 27 |
| IV | $[\text{Cr}(\text{OH})_2 \text{Cr}]^{4+}$ | 7 |
| VII | $[\text{Cr}(\text{OH})_2 \text{Cr}(\text{OH})_2 \text{Cr}]^{5+}$ | 13 |
| VIII | $[\text{Cr}(\text{OH})_2 \text{Cr}(\text{OH})_2 \text{Cr}(\text{OH})_2 \text{Cr}]^{6+}$ | 6 |

Affinity of Complexes with Collagen

The action of various complexes on collagen was investigated. In order to eliminate the factor of penetration, hide powder was used instead of hide pieces. In addition to 33 percent basic chromium chloride, 30 percent basic chromium sulfate and 20 percent basic glucose-reduced chromium sulfate in which no alkali was added were used for tannage, because these solutions contained larger quantities of sulfato and/or organo complexes than the solutions in which alkali was added. pH of tannage was 3, an approximate value of the chromium solutions, preventing the change of complexes.

The chrome contents of tanned hide powders are shown in Fig. 12. The curves obtained show the well-known influence on chrome fixation of time. Chromium was rapidly fixed to hide powders during the initial period of the tanning process and more slowly as this process continued. This trend was more marked in tanning with basic chromium chloride (Cr-Cl) than with basic chromium sulfate (Cr-SO₄) and basic glucose-reduced chromium sulfate (G-Cr-SO₄). But the chrome contents after tannage did not vary markedly with the chrome solutions used.

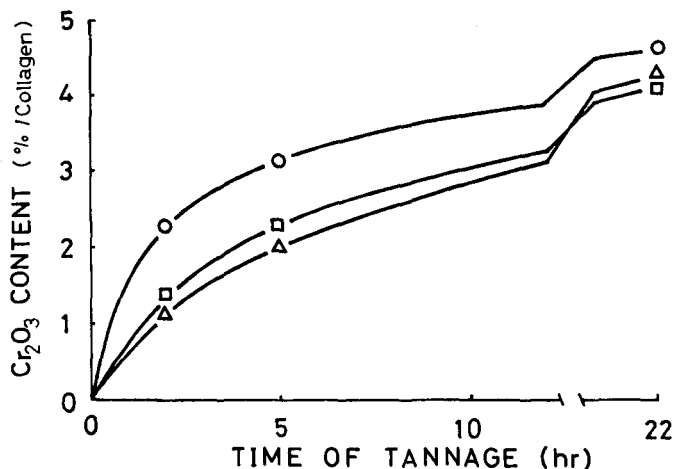


Fig. 12. Fixation of chromium by hide powder with time of tannage. Kind of chrome tanning liquors:

O: Cr-Cl Δ : Cr-SO₄ \square : G-Cr-SO₄

(a) 33 percent basic chromium chloride

The exhaustion of various complexes is shown in Fig. 13. Components II, III, and IV + V, respectively, decreased slightly, markedly, and considerably, but component I did not decrease in spite of the highest content. Exhaustion rates of each component after tannage for 22 hr were calculated. Both

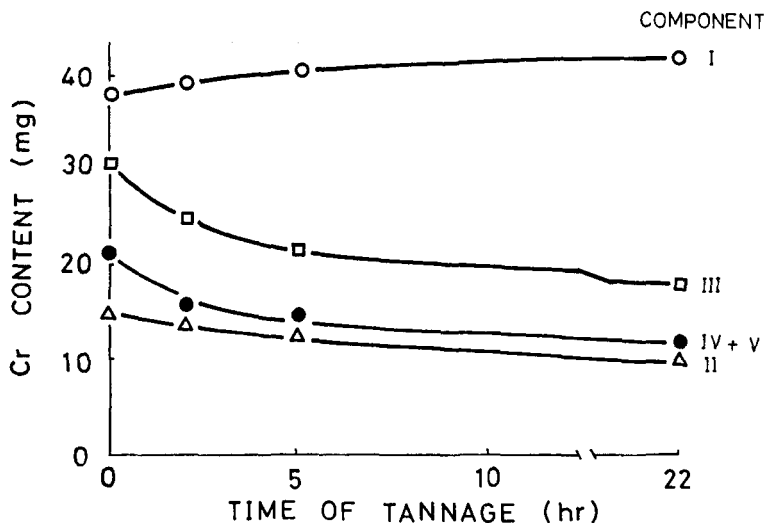


Fig. 13. Exhaustion of components in 33 percent basic chromium chloride by tannage.

components III and IV+V were about 40 percent exhaustion, and component II was about 30 percent one.

From the results obtained it is suggested that a selective combination with collagen takes place from the mixture of various chromium complexes. Components III and IV+V, consisting of polymerized hydroxo complexes, showed high affinity with collagen. Component I, hexaaquo complexes, showed no affinity in spite of the highest content.

(b) *30 percent basic chromium sulfate*

The exhaustion of various complexes is shown in Fig. 14. Components IV and VII, major components, decreased somewhat and markedly, respectively. Component V decreased only slightly in spite of a major component. The decrease of the others were slight. Part of the decrease of components I+II may be due to the change of complexes, since these components are relatively unstable complexes. The exhaustion rates of components IV and VII after tannage for 22 hr were 25 and 74 percent, respectively. The total exhaustion of components I to IV, consisting of sulfato complexes, was 37 percent of the total exhausted chromium, and that of components VI+VII, polymerized hydroxo complexes, was 52 percent.

From the results obtained it is clear that polymerized hydroxo complexes have much higher affinity with collagen than sulfato complexes.

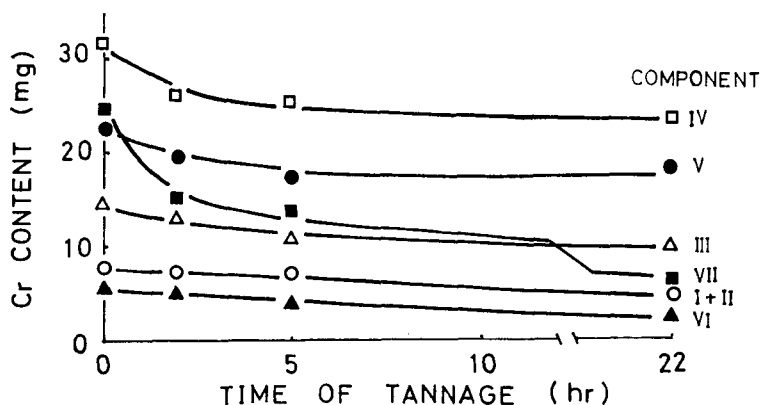


Fig. 14. Exhaustion of components in 30 percent basic chromium sulfate by tannage.

(c) *20 percent basic glucose-reduced chromium sulfate*

The exhaustion of various complexes is shown in Fig. 15. The decrease of components VI+VII was not marked because of minor components.

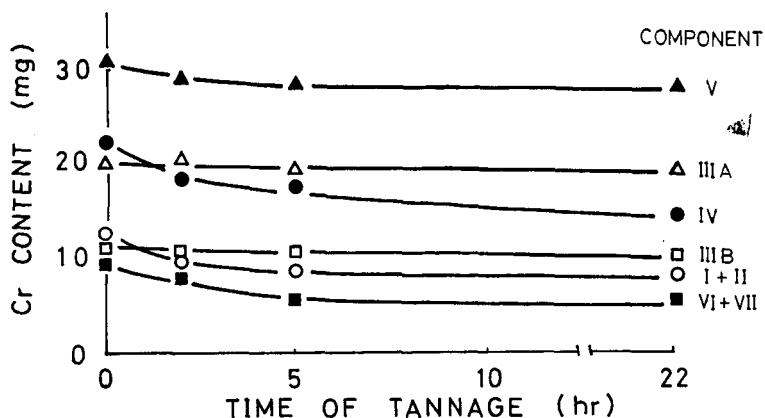


Fig. 15. Exhaustion of components in 20 percent basic glucose-reduced chromium sulfate by tanning.

Component IV decreased somewhat. Although component V was the largest quantity, its decrease was very slight. Components III A and III B hardly decreased. Components I+II decreased slightly, but part of the decrease may be due to the change of complexes. The exhaustion rate of component IV was over 30 percent, while that of components VI+VII was over 40 percent. The exhaustion amount of components VI+VII was 21 percent of the total exhausted chromium.

From the results obtained it is suggested that polymerized hydroxo complexes, components VI+VII, have the highest affinity with collagen, but formate and oxalato complexes, components V and III B respectively, have very low affinity.

Heat Resistance of Tanned Hide Powders

From the exhaustion of chromium complexes it is suggested that tanned hide powders contain various kind of complexes. The complex distribution in the tanned hide powders was calculated from the exhaustion of complexes. The hide powders tanned with basic chromium chloride (Cr-Cl) contained only hydroxo complexes, while the hide powders tanned with basic chromium sulfate (Cr-SO_4) and basic glucose-reduced chromium sulfate (G-Cr-SO_4) contained 52 and 21 percent of hydroxo complexes, respectively. The former contained sulfato complexes in addition to the hydroxo ones and the latter contained organo complexes in addition to the sulfato and hydroxo ones. Such complex distribution may be observed in tanning at other pH^0 .

Tanned hide powders with various chrome contents tanned at various pH were examined for heat resistance.

(a) *Solubility after heating in water*

The solubility of tanned hide powders after heating in water of 75°C is shown in Fig. 16. Untanned hide powder was dissolved easily by heating. Tanned hide powders of which chrome contents were less than 2 percent Cr_2O_3 /collagen also dissolved largely after heating for 24 hr, but tanned hide powders with chrome contents of more than 3 percent dissolved very slightly. After heating for 48 hr, tanned hide powders with chrome contents of less than 4 percent nearly dissolved. But as the chrome contents increased further, the solubility decreased markedly. The solubility varied little with the kind of chrome tanning solutions used.

From the results obtained it is suggested that the chrome content has a marked effect on the solubility of collagen in hot water, hydrolytic degradation, but that the kind of fixed chromium complexes has little effect.

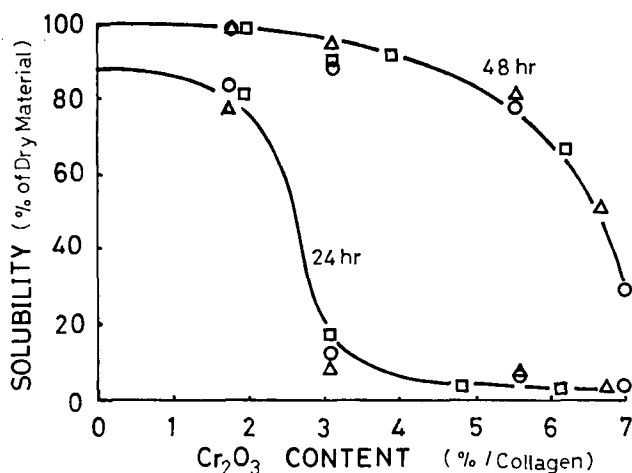


Fig. 16. Effect of the chrome content of hide powders on solubility after heating for 24 and 48 hr at 75°C in water.

Kind of chrome tanning liquors :

○ : Cr-Cl △ : Cr-SO₄ □ : G-Cr-SO₄

(b) *Solubility after heating in air*

Weight loss and soluble material of untanned hide powder after heating at 180°C for six days were 11 and 19 percent of dry material, respectively. Although the weight loss was decreased somewhat by tannage, the soluble material was decreased markedly. The absorbance of aqueous extracts of tanned hide powders after heating in air is shown in Fig. 17. The absorbance, solubility, was decreased markedly by a little fixation of chromium.

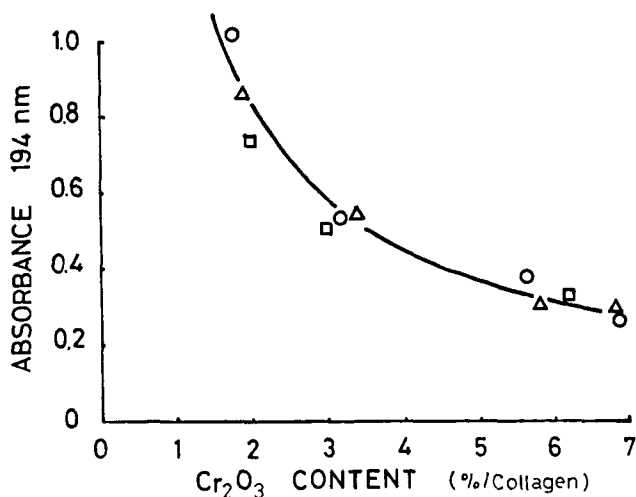


Fig. 17. Effect of the chrome content of hide powders on solubility after heating at 180°C for six days in air.

Kind of chrome tanning liquors:

○: Cr-Cl △: Cr-SO₄ □: G-Cr-SO₄

When chrome contents were around 3 percent, the solubility was a few percent. There was no appreciable difference in the solubility among the chrome tanning solutions used.

From the results obtained it is suggested that the chrome content has a marked effect on the solubility of collagen after heating in air, oxidative degradation, but that the kind of fixed chromium complexes has little effect.

(c) *Infrared spectra of tanned hide powders after heating in air*

Infrared spectra of hide powders tanned with 33 percent basic chromium chloride after heating at 180°C for ten days are shown in Fig. 18. The changes in infrared spectra occurred markedly in the region of 1000~1800 cm⁻¹ on heating. A strong band appeared at 1720 cm⁻¹ and amide III band at 1225 cm⁻¹ disappeared. These changes became smaller with increasing chrome contents. The spectrum of the tanned hide powder of about 2 percent Cr₂O₃/collagen was almost the same as that of untanned hide powder. But with the tanned hide powders of 5.6 and 7 percent chrome contents, the amide III band was observed and the band at 1720 cm⁻¹ was a medium sholder band. These changes were observed also in the hide powders tanned by chromium sulfate and glucose-reduced chromium sulfate.

The changes in infrared spectra are consistent with a partial or total breakdown of the ordered structure of collagen and the polypeptide bond.

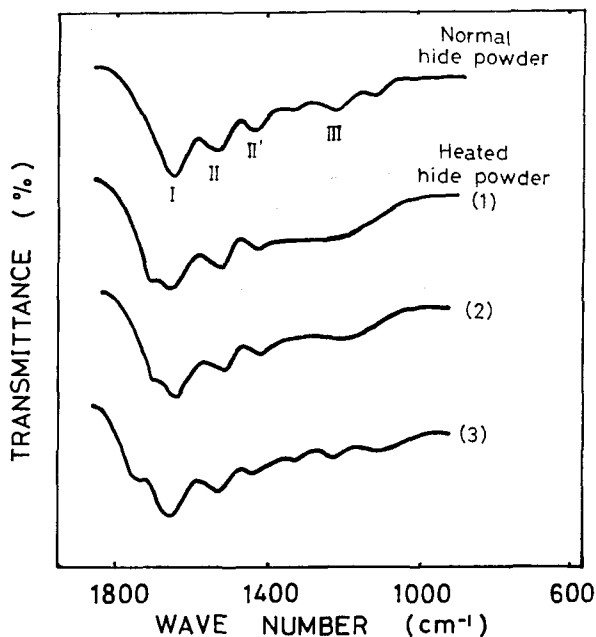


Fig. 18. Infrared spectra of hide powders tanned with 33 percent basic chromium chloride after heating at 180°C for ten days.

Chrome content (% $\text{Cr}_2\text{O}_3/\text{Collagen}$):

(1) 1.8 (2) 3.1 (3) 5.6, 7.0

Therefore, from the results obtained it is suggested that the chrome contents have a marked effect on the denaturation or degradation by heating in air, but the kind of the fixed chromium complexes has little effect.

(d) *Differential thermal analysis*

Untanned hide powders of which water content were 12 and 40 percent showed endothermal peaks of the DTA curves at 63° and 41°C, respectively. Thermograms of hide powders tanned with 33 percent basic chromium chloride of 12 percent water content are shown in Fig. 19. The tanned hide powder of low chrome content showed two peaks, but one of the peaks in lower temperature gradually became weaker with increasing chrome contents and then disappeared as the chrome content was 7 percent $\text{Cr}_2\text{O}_3/\text{collagen}$. The DTA curves shifted slightly to higher temperatures on the whole with increasing chrome contents. Although similar changes of the DTA curves were observed also from hide powders tanned with the other chrome solutions, the temperatures of peaks were a bit different with the

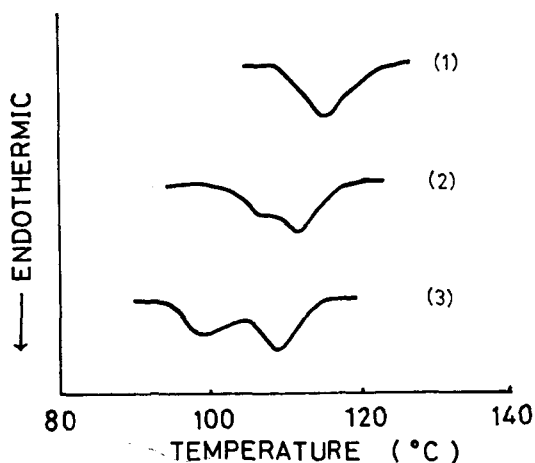


Fig. 19. Thermograms of hide powders tanned with 33 percent basic chromium chloride with water content of 12 percent.
 Chrome content (% Cr_2O_3 /Collagen):
 (1) 7.0 (2) 3.1 (3) 1.8

kind of the chrome solutions used. The relation between temperature of peaks in higher temperatures and chrome content is shown in Fig. 20 and 21.

The relation was different with water content. With low water content, the temperatures of peaks increased only slightly with increasing chrome contents, but with high water content, the temperatures of peaks increased

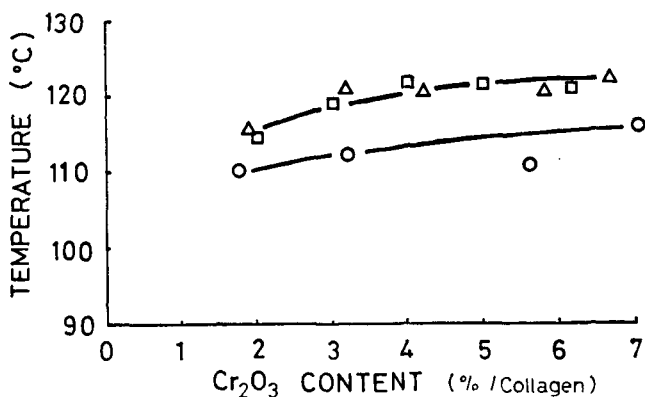


Fig. 20. Effect of the chrome content of hide powders with water content of 12 percent on DTA peak temperatures.
 Kind of chrome tanning liquors:
 ○ : Cr-Cl △ : Cr-SO₄ □ : G-Cr-SO₄

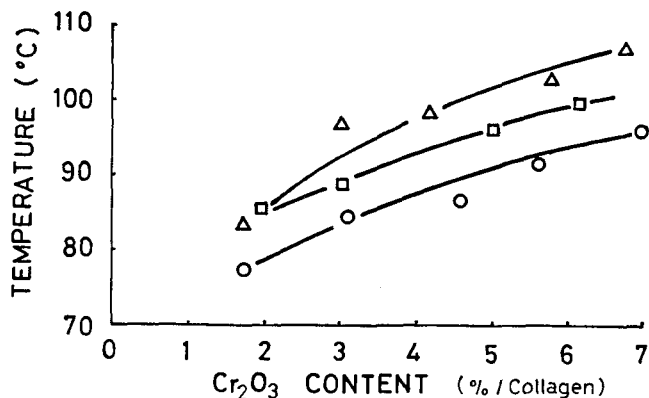


Fig. 21. Effect of the chrome content of hide powders with water content of 40 percent on DTA peak temperatures.

Kind of chrome tanning liquors:

○: Cr-Cl △: Cr-SO₄ □: G-Cr-SO₄

markedly. In the region of chrome contents from 2 to 7 percent Cr₂O₃/collagen, the temperatures of peaks were roughly 110~120°C and 75~110°C with water contents of 12 and 40 percent, respectively. The temperatures were distinctly affected by the kind of chrome solutions used. Basic chromium sulfate resulted in higher temperatures, which was more marked with high water content than with low water content. The temperatures of the hide powders tanned with basic chromium sulfate were higher than those of the hide powders tanned with basic chromium chloride by around 5° and 10°C with water contents of 12 and 40 percent, respectively.

The changes in the DTA curves are due to a thermal denaturation of collagen. Therefore, it is suggested that the chrome fixation has a marked effect on the denaturation of collagen by heating and that the kind of the fixed chromium complexes also has a considerable effect. Sulfato complexes may result in higher thermal stability than hydroxo complexes. Water content seems to have a effect on structural stability of collagen during heating.

Summary

The composition of complexes in chrome tanning liquors was studied by gel filtration and ion-exchange chromatography. 33 percent basic chromium chloride was separated into six components, while 33 percent basic chromium sulfate was separated into eight components; 33 percent basic glucose-reduced chromium sulfate was separated into nine components. There were large quantities of polymerized hydroxo complexes in the chromium

chloride, while there were considerable and small quantities of hydroxo complexes in the chromium sulfate and glucose-reduced chromium sulfate, respectively. The chromium sulfate contained low-charged and small-sized sulfato complexes in considerable quantity, while the glucose-reduced chromium sulfate contained formate and oxalato complexes as organo complexes.

The affinity of complexes for collagen was studied by using hide powder; among the various complexes, hydroxo complexes had the highest affinity and sulfato complexes corresponding to di- μ -hydroxo- μ -sulfato dichromium ones had considerable affinity.

The denaturation of tanned hide powders through heating was studied by physical and chemical analyses. The heat resistance of the tanned hide powders was more markedly affected by the quantity of chromium complexes than by their types.

Acknowledgment

The author expresses his thanks to Dr. Yukichi SAKIMOTO, Professor Emeritus of Hokkaido University, who has kindly given invaluable advice and encouragement.

Literature Cited

1. SLABBERT, N. T.: Composition of chromium (III) complexes in chromium sulfate tanning liquors, Paper presented at the I.U.L.T.C.S. conference, Barcelona, Oct. 1975. *Das Leder*, 27: 24-26. 1976
2. BALASULBRAMANIAN, N., JANAKIRAMAN, M. N., RAMASWAMI, T. and RAMASWAMY, D.: Composition of chrome tanning salts and their affinity to collagen, Paper presented at the I.U.L.T.C.S. conference, Hamburg, Sep. 1977. *Das Leder*, 29: 10-11. 1978
3. TAKENOUCHI, K. and SAKIMOTO, Y.: Studies on chrome tan Liquor (3) Analysis of chromium (III) solutions by ion-exchange and gel filtration chromatography, *Hikaku Kagaku*, 22: 77-86. 1976
4. TAKENOUCHI, K.: Composition of complexes in glucose-reduced chrome tanning liquors and their affinity to collagen, *J. Amer. Leather Chem. Ass.*, 75: 150-166. 1980
5. TAKENOUCHI, K. and SAKIMOTO, Y.: Studies on chrome tan liquor (5) Infrared spectra of masked chromium (III) complexes, *Hikaku Kagaku*, 23: 131-138. 1977
6. KAWAMURA, A., WADA, K., UEHARA, K. and TAKATA, E.: Studies on chrome tanning liquor by gel chromatography and electrophoresis, *Hikaku Kagaku*, 22: 198-194. 1977
7. LASWIC, J. A. and PLANE, R. A.: Hydrolytic polymerization in boiled chromic solution, *J. Amer. Chem. Soc.*, 81: 3564-3567. 1959
8. NAKAMOTO, K., FUJITA, J., TANAKA, S. and KOBAYASHI, M.: Infrared spectra

- of metallic complexes. IV. Comparison of the infrared spectra of unidentate and bidentate metallic complexes, *J. Amer. Chem. Soc.*, **79**: 4904-4908. 1957
9. KÜNTZEL, A. and MAHDI, H.: Detection and separation of the chromium compounds found together in green chromium sulfate solutions by paper and column chromatographic ion-exchange, *Das Leder*, **21**: 123-131. 1970
 10. THEIS, E. R., SERFASS, E. J. and CLARK, A.: Spectrophotometer investigations of chromium salts. I. Oxalato chromium compounds, *J. Amer. Leather Chem. Ass.*, **41**: 401-420. 1946
 11. SERFASS, E. J. and THEIS, E. R.: Spectrophotometer investigations of chromium salts IV. Penetration compounds formed with acetic, formic, tartaric, citric, and sulfuric acids, *J. Amer. Leather Chem. Ass.*, **41**: 206-226. 1948
 12. FUJITA, J., MARTELL, A. E. and NAKAMOTO, K.: Infrared spectra of metal chelate compounds VI. A normal coordinate treatment of oxalato metal complexes, *J. Chem. Phys.*, **36**: 324-331. 1962