Exploring on the Oxidation Approach of Chromium (III) into Chromium (VI) by Unsaturated Lipoids in Leather

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Abstract: While breaking the frame of traditional leather-making process and taking a new method, this paper explored the influence of the double bonds of unsaturated lipoids on the level of chromium (VI) in chrome-tanned leather. The following parameters were controlled during the experiment: temperature, humidity, time and the pH value, which were strengthened compared to the conditions of leather-making process. By checking the iodine value and peroxide value of the lipoids regularly and determining the changed structure with infrared spectrum, the experiment will demonstrates the oxidation mechanism of chromium (III) to chromium (VI) by unsaturated lipoids in chrome-tanned leather.

Keywords: unsaturated lipoids, chromium (VI), iodine value, peroxide value.

1. Introduction

The chromium (VI) found in leather has been a serious trouble in the leather-making industry. The causes of Cr (VI) in leather have become the topic concerned by worldwide leather technologists. There are various opinions about the causes of the Cr (VI) in leather, but up to now the authoritative viewpoints are not formed yet. However it is undisputed that fatliquors from unsaturated oils can accelerate the production of the Cr (VI) in leather. Some articles pointed out that unsaturated lipoids are easy to be oxidized in the air and produce hydrogen peroxides which can oxidize the Cr (III) to Cr (VI) \(^1\)\(^2\). Both fatliquors which have one or more double bonds and fatty acids which have been esterified have positive effects on the formation of Cr (VI), especially the sulfited fish oil and sulfonic oil \(^3\). Some experiments showed that: the Cr(VI) content is lower than the request limit (3mg/kg) in leather which has not been fatliquored or fatliquored not by the unsaturated lipoids or their esters, while the Cr(VI) content (23-35mg/kg) is far higher than the request limit (3mg/kg) in leather which fatliquored by single or poly unsaturated lipoids\(^4\).

In the past research the causes of Cr (VI) were all studied in the traditional leather making
process in which there were many interferential factors. So it is difficult to give exact answers to the influence of the unsaturated lipoids on the Cr (VI) content in leather. Moreover the oxidation mechanism of the Cr (III) to Cr (VI) and the structure change of the oil during the oxidation have not been explored clearly yet. Therefore in order to solve the above questions we try to make some innovations in our investigations:

(1) Breaking the frame of traditional leather-making process, simulating the conditions of the leather making process and selecting the sponge as carrier instead of leather to eliminate interferential factors which affect the studies.

(2) In our investigations, the content of the Cr (VI) and the corresponding iodine value and peroxide value of the oil were determined at regular intervals, which is helpful to make clear the oxidation process and the reacting mechanism of unsaturated lipoids and chromium (III).

(3) Focus on the double bond of the lipoid. Instead of speculating on the chemical reactions which might happened, we studied the functions of the double bonds and the related reactions happened during the oxidation of the Cr (III) to Cr (VI) by means of experiment. From this point we chose soybean oil, peanut oil, and pure oleic acid to be our research objects, of which the main components are oleic acid and linolic acid. Oleic acid and linolic acid are representative lipoids which have one and two double bonds individually.

In our experiment sponge was employed as a reacting carrier. Because sponge has large specific surface area due to its porous character which is similar to the physical fabric of the leather. The large specific surface area could enlarge the contact surface between the Cr (III), the oil and the air, therefore the oil and Cr (III) in the sponge could be oxidized efficiently. The sponge used in the experiment is a kind of pliable polyurethane which has simple chemical constitution and is stable enough not to affect the analysis of the Cr (VI), the peroxide value and iodine value of the oil under the condition of the experiment \([5]\).

2. Experimental

2.1 Experimental Process and Method (the following experiments were carried out synchronously)

2.1.1 Experiment of Oleic Acid System

(1) Experiment of oleic acid system 0

Cut the sponge into small pieces and dipped them into distilled water to damp-dry state, then took them out and put them into oleic acid until they were saturated by the acid. After that these saturated sponge was placed in the sun for four hours. The following operations were taken as step(3).

(2) Experiment of oleic acid system 1

Cut the sponge into small pieces and dipped them into oleic acid, then placed these saturated
sponge in the sun for two hours. After that these sponge was dipped into the prepared chrome tanning agents (4g/L, measured by Cr$_2$O$_3$) to absorb enough chromium sulphate, and then was taken out and placed in the sun for four hours. The following operations were taken as step (3).

(3) Experiment process
Put oleic acid system 0 and system 1 into the thermostat and humidistat conditions with temperature 55°C and humidity 17%. After five days, the iodine value and peroxide value of the oils in system 0 and system 1 as well as the Cr (VI) content were determined for the first time. From then on these items were analyzed every three days. To understand the changed structure of the oil, we make infrared analysis of the oleic acids in pure state, system 0 and 1.

2.1.2 Experiment of Peanut Oil System
The sample preparation for peanut oil system 0 and system 1 and the experiment process were all the same with test 2.1.1, except that the oleic acid was replaced by peanut oil.

2.1.3 Experiment of Soybean Oil System
The sample preparation for soybean oil system 0 and system 1 and the experiment process all the same with test 2.1.1, except that the oleic acid was replaced by soybean oil.

2.1.4 Control Test
To check the chromium (VI) content coming from oxidation of chrome (III) by designed experiment without unsaturated lipoids, we simply dipped the sponge into chrome tanning agents in control test. Namely: cut the sponge into small pieces and dipped them into the prepared chrome tanning agents (4g/L, measured by Cr$_2$O$_3$) to absorb enough chromium sulphate, and then the sponge was taken out and placed in the sun for four hours. The following operations were taken as 2.1.1 (3).

2.1.5 The extraction of the oil in the sponge
The oleic acid, peanut oil and soybean oil used in the experiment were extracted by means of SuoShi Extraction Method. Namely the lipoids were extracted by ethanol in a extracting instrumentation at 75°C and the ethanol was recycled after extraction. Then the lipoids were put into the drying oven (50°C) until constant weight was obtained, and thus the determination of the iodine value and peroxide value of the lipoids could be carried out.

To prove whether oil extraction has any effect on the analysis of the oil parameters, we squeezed out the three kind of oils in system 0 from the sponge and put it into drying oven (50°C) until constant weight was obtained. Then the peroxide value and iodine value of the oil were determined. At the same time, we sampled the same oils which were extracted by means of SuoShi Extraction Method and became constant weight, then determined the peroxide value and iodine value of the oils.

Note: The chromium power and the lipoids were analyzed and there is no Cr (□) existed.

2.2 Analysis and Determination
2.2.1 Determination of the Iodine Value of the Oil [6]
(1) Preparation of Wijs solution
7.9g iodine trichloride and 8.7g iodine was dissolved into acetic acid respectively. Put together the two solutions and added acetic acid to 1000ml, then the solution was stored in the dark-brown bottle.

(2) Determination of the iodine value
A given amount of oil ($W_2$) which was extracted and has become constant weight was weighed accurately and put into a clean and dry flask, 20ml trichloromethane was added to dissolve the oil, as soon as the 25ml Wijs solution was joined, the bottle lid was plugged (to avoid the volatilization of the iodine, both bottle lid and bottle neck were smeared with potassium iodide). The solution was well shaken up and placed in the dark for 50min at the room temperature. When time is up 20ml potassium iodide (15%) and 100ml distilled water was added immediately. 0.1N sodium thiosulfate standard solution was used to titrate the solution until the light yellow solution was obtained, then 1ml starch indicator (0.5%) was added. Continue to titrate the solution until the blue color was disappeared.

The control test was carried out under the same condition with the above, except that the sample oil was not used.

(3) Result display
The iodine value of the sample oil was calculated according to formula (1):

\[ \text{Iodine Value} = \left[ (V_2-V_1) \times N \times 0.1269 / W \right] \times 100 \]  
(1)

In the formula:
$V_2$—the consuming volume of the sodium thiosulfate standard solution in control test, ml ;

$V_1$—the consuming volume of the sodium thiosulfate standard solution by sample oil, ml ;

$W$—the quality of the oil, g ;

$N$—the concentration of the sodium thiosulfate standard solution, mol/L ;

0.1269—the gram value of iodine equivalent to per-mol sodium thiosulfate ;

2.2.2 Determination of the Peroxide Value of the Oil [7]
(1) Reagents
Trichloromethane- acetic acid solutions: 40ml trichloromethane and 60ml acetic acid was fully mixed;
Saturated potassium iodide solution: 10g potassium iodide was dissolved into 5ml distilled water and stored in the dark-brown bottle;
0.01N sodium thiosulfate standard solution: 10ml sodium thiosulfate standard solution (0.1N) was put into a 100ml measuring flask and distilled water was added to the calibration tails;
0.5% starch indicator: 0.5 g starch was dissolved into 100g distilled water which was heated up to boiling, cooled and deposited, the upper solution was taken as the indicator;

(2) Determination of the Peroxide Value of the oil
1) Sampling
The quality of the oil sample was weighed according to table 2-1;

| Table 2-1 |
Estimated peroxide value (mg oxygen/kg oil) | Quality of the oil sample, g
---|---
≤ 96 | 5.0-2.0
96-160 | 2.0-1.2
160-240 | 1.2-0.8
240-400 | 0.8-0.5
≥ 400 | 0.5-0.3

2) Determination

The oil which has been extracted and become constant weight was weighed accurately according to table 2-1 and put into a 250ml measuring flask, 30ml Trichloromethane-acetic acid solution was added and shaken up to dissolve the sample oil. Then added 1ml saturated potassium iodide solution and put on the lid immediately. Shook the solution and placed it in the dark for 5min, then 75ml distilled water was added. Shook it again and 0.01N sodium thiosulfate standard solution was used to titrate the solution until the light yellow solution was obtained, then 1ml starch indicator (0.5%) was added. Continue to titrate the solution until the blue color was disappeared.

The control test was carried out under the same condition with the above, except that the sample oil was not used.

(3) Result display

According to formula (2), the result was expressed as the milligram value of the active oxygen per-kilogram oil (mg oxygen/kg oil).

\[
\text{Peroxide Value (mg oxygen/kg oil)} = \left[\left( \frac{V_1}{V_0} \right) \times N/W \right] \times 8 \times 1000 \ldots (2)
\]

In the formula:

- \(V_1\) - the consuming volume of the sodium thiosulfate standard solution by the sample oil, ml;
- \(V_0\) - the consuming volume of the sodium thiosulfate standard solution in control test, ml;
- \(N\) - the concentration of the sodium thiosulfate standard solution, mol/L;
- \(W\) - the quality of the oil, g.

### 2.2.3 Determination of Cr (VI) Level in extracting liquid from sponge [8]

(1) Principle

The chromium (VI) reacted with Diphenylcarbazide (DPC) in acidic conditions and produced mauve complex compounds which could react with p-methyl benzene sulfonic acid and formed complex compounds with larger molecular weight. Isoamyl alcohol was employed here to extract the complex compounds which thereafter lay in the organic phase. By this means the chromium
(VI) could be separated with the impurities that might exist in the solution. The Cr (VI) content was measured by a spectral photometer at 540nm and the amount of Cr (VI) was calculated by using a calibration curve.

(2) Reagents
The reagents used in the experiment are of analytical quality and the water is distilled water or de-ionized water.

Isoamyl alcohol; p-methyl benzene sulfonic acid, 50g/L; sulfuric acid: 10%;
1,5- diphenylcarbazide solution: 1.0g 1,5- diphenylcarbazide was dissolved into 100ml acetone, then a drop of acetic acid was added to make the solution acidic.

Note: the 1,5- diphenylcarbazide solution was stored in dark-brown bottle and kept at 2°C-8°C without light, which is usable for 14 days. The appearance of pink color indicates the deterioration of the solution which was not usable.

Potassium bichromate (K$_2$Cr$_2$O$_7$): dried at (102±2) °C for (16±2) h.

Cr (VI) standard stock solution: 2.829g potassium bichromate (K$_2$Cr$_2$O$_7$) was dissolved into 1000ml distilled water and there was 1mg Cr (VI) (as potassium bichromate) in 1ml solution.

Chromium (VI) standard solution: 1ml Cr (VI) standard stock solution was diluted to 1000ml with distilled water, and there was 1µg Cr (VI) (as potassium bichromate) in 1ml solution.

(3) Experiment process
1) A given amount of sponge was taken out of the thermostat and humidistat and was cut into small chippings. Put these chippings into a 250ml conical flask, and then added 100ml distilled water to the flask. Placed the conical flask into an oscillator and kept it shaking for two hours. After two hours 10ml solution was sucked by a suction pipette and added to a 50ml measuring flask, then 10ml distilled water and 2ml sulfuric acid was added. The mixed solution was well shaken up and 1ml 1,5-diphenylcarbazide solution was added. Continue to shake the solution for 2min and the solution was laid quietly for 3min. Then 4ml p-methyl benzene sulfonic acid was added accurately and the solution was shaken up well. Then 10ml isoamyl alcohol was added accurately and the solution was shaken up again. After that the solution was transferred to a separating funnel, laying and stratifying. 20min later, the water phase was leaked out and a small piece of absorbent cotton was stuffed into the neck of the funnel. Then the organic phase was filtrated, 3-4 drops per-minute. The control reagent was used as the parallel contrasting sample. Optical density of the organic phase was measured by a spectral photometer at 540nm in a 2cm color comparison container and the amount of Cr (VI) was calculated by using a calibration curve.

2) Control reagent
10ml distilled water (replaced the sample solution) was sucked by a suction pipette and added to 50ml measuring flask. Then step 1) was repeated. The filtrate of the organic phase was used as
the control reagent.

3) Drawing of standard calibration curve

0ml, 1.0ml, 2.0ml, 3.0ml, 4.0ml, 5.0ml, 6.0ml chromium (VI) standard solution was sucked by
suction pipettes respectively and put into 50ml measuring flask. Distilled water was added to 10ml
in each flask which replaced the sample solutions. And then step 1) was repeated. Control reagent
was used as contrasting reagent to determine the optical density. The quality of the Cr (VI) in
chromium (VI) standard solution acted as horizontal ordinate and the optical density acted as the
vertical ordinate which together constituted a beeline through the zero. The standard calibration
curve changed with the change of spectral photometer and color comparison container.

Note: in the experiment 2cm color comparison container is suitable.

4) Result display

The Cr (VI) content was calculated according to formula (3):

\[
Cr(\text{VI}) = \frac{A}{k}
\]  

(3)

In the formula:

\(Cr(\text{VI})\) - the quality of Cr (VI) in the chromium (VI) standard solution, \(\mu g\);

\(A\) - optical density of the Cr (VI);

\(K\) - the rate of slope of the standard calibration curve, \(\frac{A}{\mu g}\).

2.2.4 Spectrums of oleic acid analyzed by Fourier Transform Infrared (FTIR)

The original oleic acid and oleic acid system 0 and system1 were analyzed on the 8 day of the
experiment by Fourier Transform Infrared (FTIR) to observe the changed structure of the lipoid.

3.  Results and Discussion

3.1 Results and Discussions of Different Oil Systems

3.1.1 The Results of Oleic Acid System

The results of test 2.1.1 are shown in table 3-1 and figure 3-1 to 3-2:

<table>
<thead>
<tr>
<th>Time/d</th>
<th>0</th>
<th>5</th>
<th>8</th>
<th>11</th>
<th>14</th>
</tr>
</thead>
<tbody>
<tr>
<td>System 0 Peroxide value  (mg oxygen/kg oil)</td>
<td>0</td>
<td>9.6</td>
<td>82.4</td>
<td>188.8</td>
<td>49.6</td>
</tr>
<tr>
<td>System 0 Iodine value  /gl2/100g oil</td>
<td>122.7</td>
<td>110.5</td>
<td>104.5</td>
<td>98.5</td>
<td>69.4</td>
</tr>
<tr>
<td>System 1 Peroxide value  (mg oxygen /kg oil)</td>
<td>0</td>
<td>18.4</td>
<td>123.2</td>
<td>257.6</td>
<td>251.2</td>
</tr>
<tr>
<td>System 1 Iodine value  /gl2/100g oil</td>
<td>122.7</td>
<td>105.7</td>
<td>99.7</td>
<td>91.3</td>
<td>65.1</td>
</tr>
</tbody>
</table>
3.1.2 Results of Peanut Oil System
The results of test 2.1.2 are shown in table 3-2 and figure 3-3 to 3-4:

### Table 3-2 Results of Peanut Oil System

<table>
<thead>
<tr>
<th>Time/d</th>
<th>0</th>
<th>5</th>
<th>8</th>
<th>11</th>
<th>14</th>
</tr>
</thead>
<tbody>
<tr>
<td>System 0 Peroxide value (mg oxygen/kg oil)</td>
<td>0</td>
<td>105.6</td>
<td>524.8</td>
<td>737.6</td>
<td>364.8</td>
</tr>
</tbody>
</table>
### 3.1.3 Results of Soybean Oil System

The results of test 2.1.3 are shown in table 3-3 and figure 3-5 to 3-6:

<table>
<thead>
<tr>
<th>Time/d</th>
<th>System 0 Peroxide Value (mg oxygen/kg oil)</th>
<th>System 1 Peroxide Value (mg oxygen/kg oil)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>2.9</td>
</tr>
<tr>
<td>5</td>
<td>32.8</td>
<td>580.0</td>
</tr>
<tr>
<td>8</td>
<td>44.0</td>
<td>897.6</td>
</tr>
<tr>
<td>11</td>
<td>163.2</td>
<td>885.6</td>
</tr>
<tr>
<td>14</td>
<td>106.4</td>
<td>72.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.9</td>
</tr>
</tbody>
</table>

**Table 3-3 results of soybean oil system**
<table>
<thead>
<tr>
<th>System 0 Iodine value/gI/100g oil</th>
<th>138.6</th>
<th>118.3</th>
<th>110.8</th>
<th>94.9</th>
<th>34.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>System 1 Peroxide value (mg oxygen /kg oil)</td>
<td>0</td>
<td>78.4</td>
<td>178.4</td>
<td>353.6</td>
<td>330.4</td>
</tr>
<tr>
<td>System 1 Iodine value/gI/100g oil</td>
<td>138.6</td>
<td>109.6</td>
<td>104.2</td>
<td>85.6</td>
<td>26.6</td>
</tr>
<tr>
<td>System 1 Cr(VI)/µg</td>
<td>0.0</td>
<td>3.6</td>
<td>5.5</td>
<td>6.3</td>
<td>8.8</td>
</tr>
<tr>
<td>Cr(VI)/µg in control test</td>
<td>0</td>
<td>1.2</td>
<td>3.3</td>
<td>4.0</td>
<td>5.8</td>
</tr>
</tbody>
</table>

### Figure 3-5 Iodine value and peroxide value of soybean oil system

![Iodine value and peroxide value of soybean oil system](image)

### Figure 3-6 Cr(VI) contents of soybean oil system

![Cr(VI) contents of soybean oil system](image)

#### 3.1.4 Results of Control Test

The results of test 2.1.4 are shown in table 3-4 and figure 3-7:
3.1.5 Influence of Oil Extraction on the Determination of the Oil

In order to prove whether the oil extraction had any effects on the determination of the lipoids, we analyzed the peroxide value and iodine value of the oils before and after extraction on the 8 day of the experiment. The results are shown in table 3-5:

Table 3-5 results of before and after extraction on the 8 day

<table>
<thead>
<tr>
<th>Lipoids Determination</th>
<th>Soybean oil (before extraction)</th>
<th>Soybean oil (after extraction)</th>
<th>Peanut oil (before extraction)</th>
<th>Peanut oil (after extraction)</th>
<th>Oleic oil (before extraction)</th>
<th>Oleic oil (after extraction)</th>
</tr>
</thead>
<tbody>
<tr>
<td>System 0 Peroxide value (mg oxygen /kg oil)</td>
<td>40.8</td>
<td>44.0</td>
<td>518.4</td>
<td>524.8</td>
<td>78.4</td>
<td>82.4</td>
</tr>
<tr>
<td>System 0 Iodine value/gI2/100goil</td>
<td>111.3</td>
<td>110.8</td>
<td>112.4</td>
<td>111.5</td>
<td>119.4</td>
<td>118.5</td>
</tr>
</tbody>
</table>

3.1.6 Contrasting of Chromium (VI) Contents between Different Systems

The chromium (VI) contents of different oil systems are shown in table 3-6 and figure 3-8:

Table 3-6 chromium (VI) contents of different systems

<table>
<thead>
<tr>
<th>t/d systems</th>
<th>0</th>
<th>5</th>
<th>8</th>
<th>11</th>
<th>14</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control test/µg</td>
<td>0.0</td>
<td>1.2</td>
<td>3.3</td>
<td>4.0</td>
<td>5.8</td>
</tr>
<tr>
<td>Oleic acid system/µg</td>
<td>0.0</td>
<td>3.2</td>
<td>6.4</td>
<td>8.2</td>
<td>9.9</td>
</tr>
<tr>
<td>Peanut oil</td>
<td>0.0</td>
<td>2.9</td>
<td>4.7</td>
<td>6.1</td>
<td>7.9</td>
</tr>
</tbody>
</table>
3.1.7 Discussions

The above tables and figures revealed that:

(1) In order to make the oils pure enough to be determined accurately, we use ethanol to extract the oils in the sponge at 75°C. Table 3-5 showed that there is little difference of peroxide value and iodine value between the determinations of the before and after extracted oils. Therefore the extraction does not influence the accuracy of the determinations.

(2) In the oxidation process the peroxide value of the three lipoids first gradually raises and then after a maximum it goes down. This is because the oxidation of the lipoids is a dynamic balancing, therefore the production of the peroxides, the decomposition and the polymerization of the lipoids occurred simultaneously at the first stage of the oxidation. When the peroxides reach a given point, the decomposition and polymerization of the lipoids would accelerate rapidly which results in the decrease of the peroxide value at the anaphase of the oxidation.[9]

(3) The increasing extent of the peroxide values of three lipoids in system 1 is larger than that in system 2, which indicates that the lipoids are easier to be oxidized at the presence of chromium ions. This is perhaps because chromium is a kind of transition metal which has several single d orbit electrons and can accelerate the electron transfer. Therefore it serves as catalyst in many chemical reactions[10]. So in the oxidation process, chromium ions might act as catalyst to accelerate the oxidation of the lipoids which result in the larger increasing extent of the peroxide in system 1.

(4) Generally speaking, in the oxidation process the iodine values of the three lipoids are on the
downtrend though the drop value is small. The increase of the peroxide value does not have strictly inverse ratio to the decrease of the iodine value in the oxidation process of the lipoids and large increase of the peroxide value is only accompanied by small drop of the iodine value. Therefore the primary conclusion is obtained that: the main oxidation does not take place at the double bond of the lipoids, namely it is not that the double bond was opened up and formed peroxide, otherwise the increase of the peroxide value would have inverse ratio to the decrease of the iodine value.

(5) On the whole, Cr (VI) contents in the oleic acid system are the highest followed by soybean oil system and the peanut oil system. While Cr (VI) contents in single basic chromium sulphate solutions are the lowest. This indicates that: Unsaturated lipoids could accelerate the production of the Cr (VI). The level of the Cr (VI) has roughly direct ratio to the iodine value of the lipoid and the higher the iodine value, the greater the Cr (VI) content is. However oleic acid is an exception whose iodine value is lower than that of soybean oil and peanut oil, while the Cr (VI) content in which is the highest. That is because oleic acid is analytical quality and has no natural antioxidant which has been eliminated in purification process, while soybean oil and peanut oil are mixtures of several natural lipoids and have natural antioxidant which has negative effects on the oxidation ability of the lipoids.\textsuperscript{[11][12]}

3.2 Analysis of the oleic acid system by Fourier Transform Infrared (FTIR)

The oleic acid systems were analyzed by Fourier Transform Infrared (FTIR), the spectrums of the samples are shown in Figure 3-9 to 3-11;

Figure 3-9 spectrum of original oleic acid
Figure 3-10 spectrum of oleic acid system 0
(Note : System 0 denotes the oleic acid in the sponge that was dipped into oleic acid and water )
From figure 3-9 to 3-11 the following conclusions may be drawn:

i) Contrasting between figure 3-9, 3-10, 3-11 showed that the absorbance of –OOG increases gradually at 3470 cm\(^{-1}\) which indicates that the peroxide has been formed.

ii) The absorbance of the syn-librations of the -C=C- bond decreases between 3000-3400 cm\(^{-1}\) (fig. 3-10, 3-11), while there is obviously absorbance at 1000-1200 cm\(^{-1}\) (fig. 3-10, 3-11), and the significant variation provides a useful clue that the absorbance of the trans-form librations of the -C=C- bond increases. This would imply that the syn-conformation could convert into the trans double bond conformation in the first-order oxidation stage of the lipoids.

iii) With the premises that the oxidation degree of oleic acid in system 1 is deeper than that in system 0, the following conclusions could be obtained: Figure 3-10 shows that there exists a single peak at 1179 cm\(^{-1}\) in the first-order oxidation stage but with the progress of oxidation the new peak moves slowly from 1179 cm\(^{-1}\) to 1166 cm\(^{-1}\) (Fig. 3-11) and the conversion of the syn-librations of the double bonds to the trans-librations increases. With the increasing of peroxide value, the new peak of 1166 cm\(^{-1}\) becomes more and more evident.

iv) The decreasing absorbencies of the syn-form librations and the increasing trans-form librations
at the place related to C=C bond in the spectrums showed that the main oxidation occurred not at the double bond of the lipoid but at the alpha H adjacent to the double bond. Otherwise, there should not appear both the decreasing syn-form librations and the increasing trans-form librations related to C=C bond in the spectrum. Because oxidation taking place at the double bond will form triatomic ring or four-membered ring epoxide which is a flat structure, therefore the variation between the syn and trans conformation can not exit \[13\].

4. Conclusions

(1) The main oxidation of unsaturated lipoids occurred at the alpha H adjacent to the double bond.

(2) In the oxidation process the peroxide value of the lipoid first gradually raises and then after a maximum it goes down. The increasing extent of the peroxide values of three lipoids in system 1 is larger than that in system 0 which indicates that the presence of chromium ions could accelerate the oxidation of the lipoids.

(3) The unsaturated lipoids can accelerate the chromium (VI) formation, and the level of chromium (VI) in single basic chromium sulphate solution without lipoids is lower than that in the mixtures constituted by chrome tannage and lipoids.

(4) The level of the chromium (VI) has roughly direct ratio to the iodine value of the lipoid. The higher the iodine value, the more the amount of chromium (VI) is.

(5) From above conclusions (1) to (4) we know that there are close relationship between the chromium and the unsaturated lipoids: the presence of chromium (III) ions could accelerate the oxidation of the lipoids, likewise the oxidation of the lipoids could accelerate the oxidation of chromium (III) to chromium (VI).

(6) The oxidation of the unsaturated lipoids is a complicated process. Besides rough rule in the oxidation of lipoids and chrome, the increase of the peroxide value does not have strictly inverse ratio to the decrease of the iodine value in the oxidation process of the lipoids and large increase of the peroxide value is only accompanied by small drop of the iodine value, while the peroxide value began decrease, the decomposition of the lipoids began quicken up, the iodine value had a sharp drop. This indicated that the decomposition of the lipoids affects the changing trend of the iodine value and peroxide value. At the same time anti-oxidizing agents in the lipoids has negative effects on the oxidation ability of the lipoids, thereby restrain the oxidation of chromium (III) to chromium (VI). That could be seen from the following phenomena: the chromium (VI) of the oil system in which there is anti-oxidizing agent is lower than that of the oil system without anti-oxidizing agent, though the iodine value of the former lipoid is higher than that of the latter.

References

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