Scanned

Leather Technology

5th MID SEMESTER EXAMINATION-2018

Paper:- principle of Inorganic Tannage.

Solution

Q.1 ⓐ Ans:-

In this process of tanning the pelt has been agitated in the mixture of dichromate, acid and salt solution directly. The action of acid on dichromate liberate chromic acid in the solution penetrate into the pelt and get uniformly distributed throughout the cross section of the pelt. The salt in the mixture prevents the unwanted swelling due to acid present in the solution. The reaction takes place with acid and dichromate is as follows.

$$\underset{\text{(dichromate)}}{Na_2Cr_2O_7} + \underset{\text{(acid)}}{H_2SO_4} = \underset{\text{(salt)}}{Na_2SO_4} + \underset{\text{(chromic acid)}}{H_2Cr_2O_7}$$

The chromic acid impregnated pelt are then transferred to the second bath (reduction bath) containing reducing agent like sodium thiosulphate with acid. The chromic acid gets reduced by the sulfurous acid and basic chromium compounds are formed inside the skin which tan the latter. The reaction takes place in the second bath is as follows.

ⓐ $$\underset{\text{(chromic acid)}}{H_2Cr_2O_7} + \underset{\text{(acid)}}{2H_2SO_4} + \underset{\text{(sodium thiosulphate)}}{3Na_2S_2O_3} \rightarrow \overset{\text{(BCS)}}{2Cr(OH)SO_4} + \overset{\text{(salt)}}{3Na_2SO_4} + 3S + 2H_2O$$

ⓑ excess of acid:

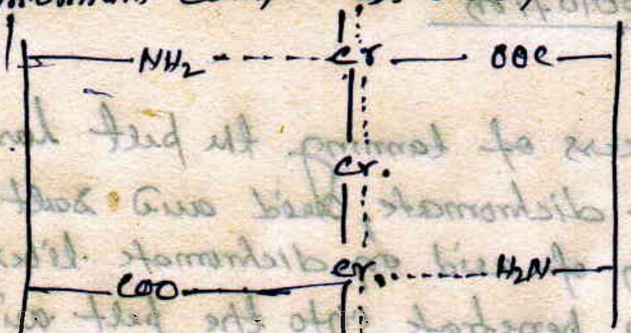
$$4H_2Cr_2O_7 + 5H_2SO_4 + 3Na_2S_2O_3 \rightarrow 8Cr(OH)SO_4 + 3Na_2SO_4 + 5H_2O$$

ⓒ excess of thiosulphate,

$$H_2Cr_2O_7 + 5H_2SO_4 + 6Na_2S_2O_3 \rightarrow 2Cr(OH)SO_4 + 3Na_2SO_4 + 3Na_2S_4O_6 + 5H_2O$$

1(b) Ans:- In the chrome tanned leather, the cross linkage with protein fibre and chrome particle are generally co-ordinated bond. This bond cannot easily break. In chrome tannage chromium causes tanning by reacting with both carboxyl and amino group of collagen.

According to complex co-ordination Theory a primary valency bond is formed between the chromium complex and carboxyl ion and a secondary valency bond between amino group of collagen and chromium complex as shown below:



Due to this linkage thermal stability of chrome tanned leather increased. and Stand boil test after chrome tanning.

Q.② Ans:—

The basicity of chrome can be defined as the percentage valence of chromium attached to hydroxyl group.

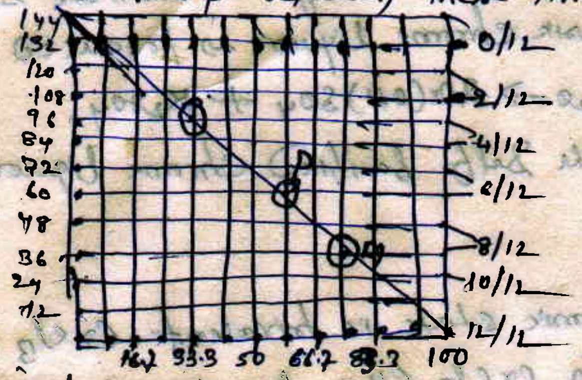
Schorlemmer or percentage basicity:— The basicity increased as more and more percent of chromium valence are attached to hydroxyl group. Chromium in the chrome liquor is trivalent and if all its three valences are attached to (OH) group, $Cr(OH)_3$ the compound is 100% basic. Similarly in $Cr_2(SO_4)_3$ is 0% basic as in this compound there is no hydroxyl group.

procter basicity:— This basicity is expressed as the gms of SO_4 combined with 52 gms of chromium, Thus the procter's basicity of the compound $Cr(OH)_3$ is 52:0 as no SO_4 group is attached with chromium. Similarly for $Cr_2(SO_4)_3$ this basicity is 52:144 and so on.

freiberg basicity:— Basicity on this Scale is expressed in term of $\frac{1}{12}$th the extent to which the SO_4 in normal Chromic Sulfate has been replaced by OH in the basic Chrome Sulfate. In this Scale normal chromic Sulfate is represented by the formula ~~$Cr_8(SO_4)_{12}$~~. $Cr_2(SO_4)_3$ multiplied by 4. means. $Cr_8(SO_4)_{12}$. This Salt has no hydroxyl group in its molecule and its basicity is 0, which is represented as $\frac{0}{12}$. As each SO_4 radical is neutralised by the addition of alkali and replaced by $(OH)_2$ the basicity of the neutralised salt increased by $\frac{1}{12}$. When all the 12 (SO_4) radicals are neutralised and replaced by $(OH)_{24}$, it is converted into Chromic hydroxide. $Cr_8(OH)_{24}$ which has the basicity $\frac{12}{12}$

All basicity between $\frac{0}{12}$ to $\frac{12}{12}$ are represented as $\left(\frac{1}{12}\right)$ as increase of 12 Freiberg basicity. Corresponds with the decrease of 12 of basicity number of the Procter system and an increase of 8.32 in Schorlemmer scale.

The relationship between these three scale is as shown by Graph.



P.S.M is the points at which precipitation starts.

Q.③ - Ans:— The Variable parameter of chrome tannage are as follows.

ⓐ Effect of pH value in chrome tanning:—

The amount of acid or alkali present in the chrome Liquor or added from outside, the tanning behaviour of chrome Liquor and quality of leather produced are well related.

ⓑ Effect of concentration:—

When Chrome Liquor is diluted, the chromium compound is hydrolysed and thereby the basicity and molecular size of the chrome complex increases even though it does not affect the basicity of liquor as whole.

ⓒ Effect of Salt:—

The effect of salt on the chrome Liquor are:

ⓐ To lower the pH value ⓑ To increase the real concentration of the chrome liquor. ⓒ To affect the nature of the chrome complex. ⓓ To change the precipitation figure of the chrome liquor.

The effects of salt on the leather are:—

ⓔ To change the chrome fixation by the collagen.

ⓕ To change the shrinkage temperature and other qualities like feel, fullness etc of the leather.

Chrome liquor is made from dichromate dissolved in minimum quantity of water in a lead lined vessel and then required quantity of Sulphuric acid is added. The chromic acid thus formed is then ~~heated~~ reacted with reducing agents with vigorous stirring. Glucose or molasses is used as a reducing agent but other

Substances like hypo, sawdust, fleshing (glue) glycerine, formaldehyde, alcohol, oxalic acid, unsaturated fatty acid etc can also be used.

When SO_2 is passed through dichromate solution without acid, a 33% basic chrome liquor is produced.

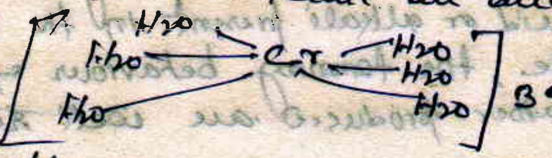
$$K_2Cr_2O_7 + 3SO_2 + H_2O \rightarrow 2Cr(OH)SO_4 + K_2SO_4.$$

Such liquor is called the self basified chrome liquor.

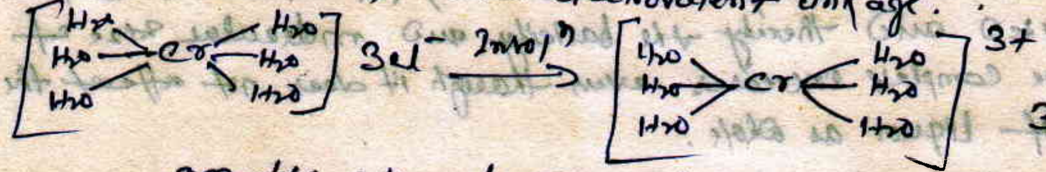
Q④ - Ans:—

Chromium in the chrome state is trivalent i.e. $CrCl_3$ but normal chrome chloride is $CrCl_3 \cdot 6H_2O$. According to Werner these water molecule attached by auxilliary valence.

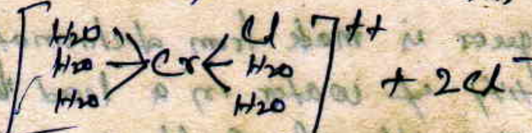
In normal chrome chloride, chloride atom are attached to chromium by primary valance forming electrovalent linkage. Where as six water molecule are attached by secondary valency



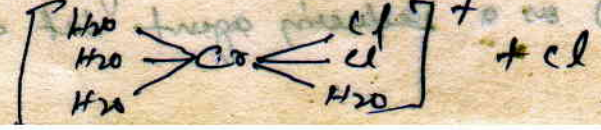
The three chlorine atoms have received each one electron from chromium to form the electrovalent linkage.



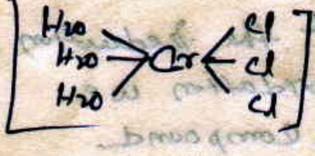
On the other hand, each of the six water molecule has shared with chromium a pair of electrons forming co-ordinate linkage. The water molecule are not therefore so easy to detached from chromium. $(Cr6H_2O)^{+++}$ is thus a complex and act as a unit. When the voilet solution of chrome chloride is heated, the solution turn green. Due to the supplied heat one water molecule of the complex gets replaced by chlorine atom with formation of the another type of chlorine called β form. To do this one chlorine atom, out of the three has given back one electron which it received from chromium previously.



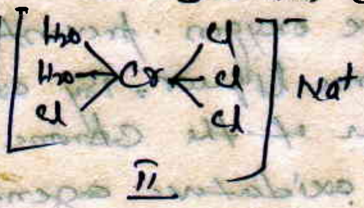
Further heating convert β-~~chrome~~ chrome chloride to γ-chrome chloride from which only one chlorine ~~an~~ ~~to~~ is out side the bracket.



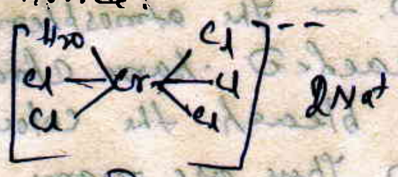
There are another four more possible types of chromium Chloride, whose formation may occur in the presence of hydro-chloric acid and sodium Chloride.



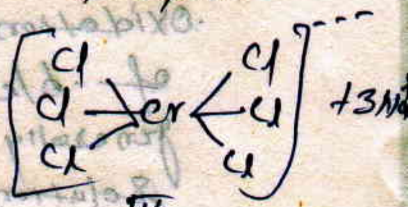
I



II



III



IV

Nomenclature of chrome co-ordination compound.

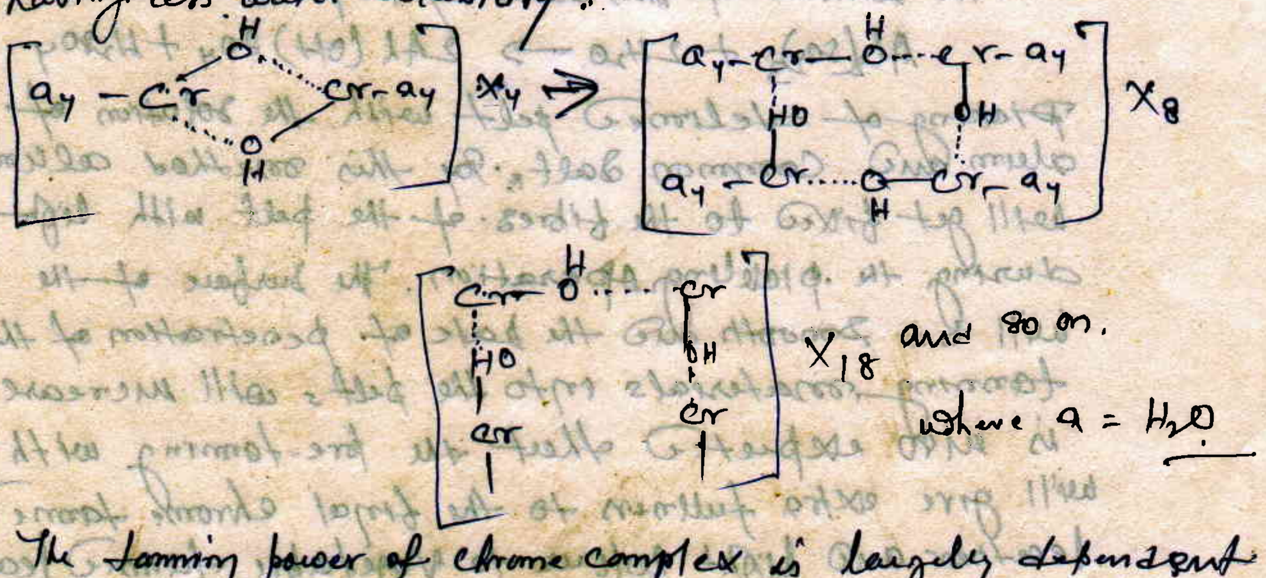
ⓐ cationic chrome compound:— The name of cationic chrome complex starts with the complexly held acid. group followed by other co-ordinated group. then comes the central element followed by the groups outside the complex. Thus B- chromic chloride is monochloropentaaquo chromic Chloride.

ⓑ No-ionic compound:— The method is same as above except that it ends with the full name of the central elements. Thus compounds I is named as ~~Sodium hexachlorocromiate~~. trichloro-triaquo-chromium.

ⓒ Anionic compounds:— The name begins with the cation outside the complex and terminate with the word chromiate. Thus compound IV is named as sodium-hexachloromiate.

Q ⑤ Ans:-

The molecular weight of chrome complexs can also be increased by polymerization. No water molecule is eliminated during polymerisation with the formation of very big complex having less water solubility.



and so on.

where $a = H_2O$

The tanning power of chrome complex is largely dependent on it's size, as smaller particle do not have tanning property as on other hand, large colloidal particles do not penetrate the collagen fibre. chrome Liquor generally used in the tanneries contain complexes with two or three Chromium atom.

Oxidation:— The atmosphere oxygen prevent the reduction of bleached basic Chrome Liquor. By oxidation we generally bleach the colour of the Chrome compound Solution. There are many oxidative agents like chlorine, hydrogen peroxide permanganate etc can be used for oxidation of basic Chromium Salt solution.

Q⑥- Ans:

ⓐ Aluminium tannage:—

For the production of glove, uppers, harness and other items of leather Alum tannage was the only method of mineral tannage before the discovery of chrome tanning. Aluminium tanning can be considered as a method of preservation, intermediate between curing and Chrome tanning. Aluminium tanning does not increase the shrinkage temperature. Moreover, the aluminium salt like other tanning agents reacts with protein giving the leather fibre a wooly appearance, which is not expected from cured hides and skin.

When alum is dissolved in water it produces in the solution free sulphuric acids as a result of hydrolysis and the aluminium sulphate gains a slight tanning power with the removal of this acid by the pelt.

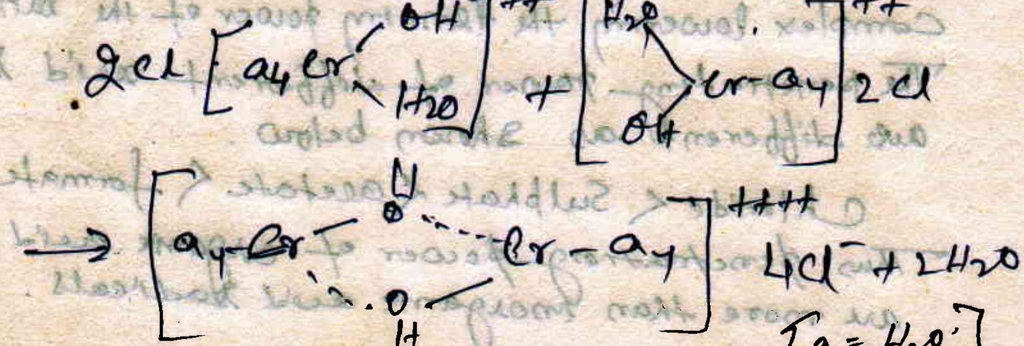
$$Al_2(SO_4)_3 + 2H_2O \rightarrow 2Al(OH)SO_4 + H_2SO_4$$

Pickling of delimed pelt with the solution of potash alum and common salt. By this method aluminium will get fixed to the fibres of the pelt with light tanning during the pickling operation. The surface of the pelt will be smooth and the rate of penetration of the stronger tanning materials into the pelts will increase. It is also expected that the pre-tanning with aluminium will give extra fullness to the final chrome tanned leather and light colour to vegetable tanned leather.

(b) Olation:—

freshly prepared chrome liquor is not so effective, after ageing this liquor certain changes take place and olation is one of them. Due to this olation molecular size of the chrome compound increases. Olation can be defined as linking of one hydroxyl group by two adjacent chromium atoms. The hydroxyl group is linked up with one chromium atom by primary valence and with next chromium by secondary valence. thus $Cr-OH\cdots Cr$

The olated hydroxyl group is under the double influence of two chromium atom. It is very firmly held in the complex. Olation is favoured by heat, increasing concentration and time. the net electric charge per chromium atom is not affected by olation as shown below.

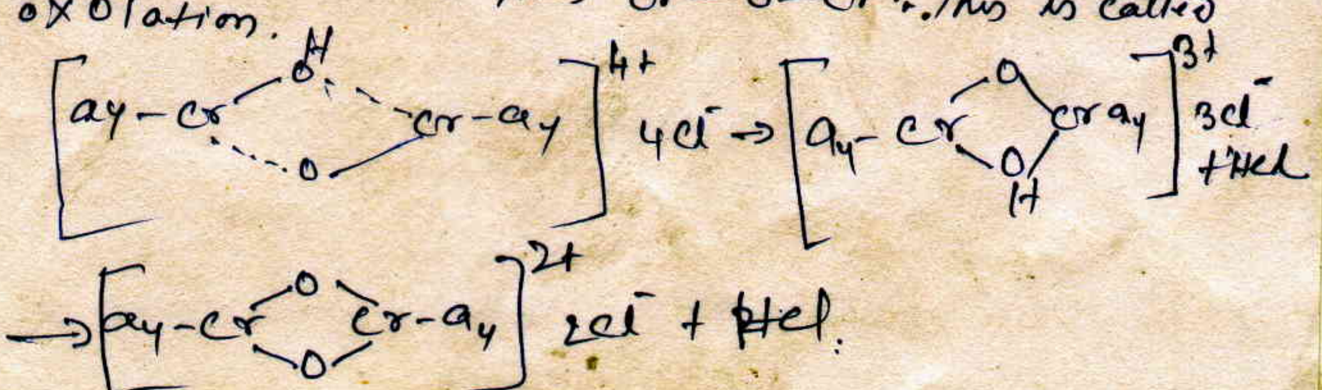


[a = H_2O]

Olation may link up more than two chromium atoms thus increasing the molecular weight of the chrome salt.

(c) Oxolation:—

When olated chrome compounds are continously heated more acid is found to be liberated and the chrome complexes become more stable than olated compounds. due to oxygen bridge between two chromium atoms. Thus $Cr-O-Cr$. This is called oxolation.

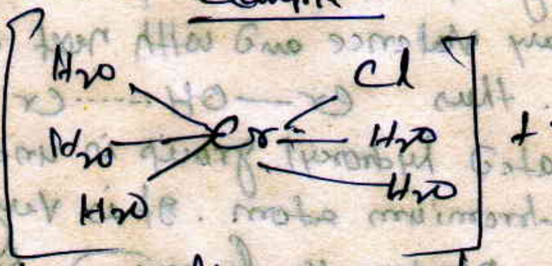


a = H_2O.

(c) Masking :-

Any organic or inorganic acid radicals inside the third bracket or complex for co-ordinate linkage with Chromium. This acid can not therefore ionise nor can it be precipitated ~~by~~ so there acid radicals thus inactive as far as chemical reaction is concerned, and can be called masked.

example



from P- Chromic Chloride, therefore. only two chlorine out side the complex, can be precipitated.

when these acid radicals penetrate into the Chrome complex lowering the tanning power of the latter. The penetrating power of different acid radicals are different as shown below.

Chloride < Sulphate < acetate < formate < oxalate.

Thus penetrating power of organic acid radicals are more than inorganic acid radicals.