The usage of modified montmorillonite to enhance the quality of leather velour

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Abstract. The paper considers the study of the possibility to use modified montmorillonite in velour production process in order to improve its quality. The adsorption of anionic black dye with velour derma has been investigated. A 16% increase was identified of the dye sorption by velour treated with the modified montmorillonite dispersion. The use of modified montmorillonite dispersion also provides additional formation of derma structure thereby increasing its strength by 11%.

1. Introduction

Today, leather velour is increasingly used for the production of clothing, footwear, haberdashery and gloves. This velour has a pile surface obtained by polishing. The velour surface also has a uniform and even color. The velour production capacity at enterprises is increasing year by year not only because of the substantial demand of consumers. Reducing the quality of leather raw materials as a whole, the presence of defects on the leather surface, spit mill after double glazing, are the main reasons for increasing the volume of velour production.

Typically, the technology of velour production differs from that one of grain leather only by semi-finished processes and operations. However, today, leather enterprises make adjustments to technology already at the stage of tanning processes. Such changes contribute to the formation of dense, low, uniform, elastic pile with multiple polishing. Polishing of velour is carried out several times with abrasive materials of different graininess. Too soft, loose semi-finished product is hard to grind. The result of this polishing is the presence of villus of different lengths on velour surface. The velour thus loses its nobility and its price decreases. Consequently, the additional formation of the volume of derma in tanning and post- tanning processes of velour production contributes to increasing its quality. The formation of the volume of derma is achieved through the use of both individual polymer compositions, mineral and organic tributaries, dispersions of natural minerals, and a combination of these materials [1-3].

The most common defect of velour is removing dye from the pile surface during operation of its products. The appearance of a defect may compromise production process and application of chemical materials used in the manufacture of grain leather. In order to obtain a high-quality velour, it is necessary to conduct a rinse after dying and use of sorbents for additional fixation of dyes. Montmorillonite is a silicate with properties of an effective sorbent. To increase the hydrophilicity of its surface, it is enough to use exchange sodium cations. As a result of such modification, the dispersion of montmorillonite acquires certain colloidal properties and allows forming derma structure.
at its various levels [1]. Most likely, the formation will contribute to additional fixation of dyes in the structure and to obtain a low and uniform pile.

The aim is to study the quality of velour, pre-treated with montmorillonite dispersion. The subject of the study is the degree of absorption of synthetic dye in the process of dying, the mechanical properties of velour and chemical interactions occurring between the dye and modified dispersion of montmorillonite.

2. Materials and Methods
Bentonite clays of the Dashukiv deposit (Ukraine) were used for the study. The content of montmorillonite in bentonite clay is 85%. Modification of montmorillonite is carried out by the introduction of sodium carbonate (5% by weight of dry mineral) into a dispersion with a concentration of mineral 100 g/l. Modification of montmorillonite with sodium carbonate leads to cation replacement of the natural metallic complex ions of the mineral with sodium ions. Such replacement contributes to the maximum level of dispersion of the mineral aggregates to its separate structural formations with a size of 0.94-1.0 nm. The presence of different particle sizes in montmorillonite modified dispersion contributes to formation of derma structure at different levels. The specific surface of montmorillonite is 700 - 840 m²/g [4].

Anionic black dye (figure 1) with a pronounced green tint was used for dying.

![Structural formula of anionic black dye](image)

**Figure 1.** Structural formula of anionic black dye (Technical Specification 6-14-767).

For further research, samples of the semi-finished chrome tanning method were used, obtained by the typical method of velour production from the bottom split of cattle. The thickness of the test samples is 1.1 - 1.2 mm. Velour samples were treated with a modified dispersion of montmorillonite in the amount of 2.5% of the mineral from the mass of semi-finished product. Fixation of the modified dispersion of montmorillonite is carried out using sodium formate in the amount of 0.4% from the mass of semi-finished product. Dispersion treatment is carried out at a temperature of 30 °C. The processing time together with the fixation process is 90 minutes. Samples of the control group (option 1) are not subject to dispersion. For lubrication will used material Provol BA («Zschimmer Schwarz GMBH Co», Germany).

In order to evaluate the effectiveness of the modified dispersion of montmorillonite to intensify the velour dying, adsorption studies were conducted and the adsorption level of dyes was determined. The adsorption of dye on a semi-finished product treated with a modified dispersion of montmorillonite is based on the optical density parameters of dye solutions obtained using photoelectrocolorimetric method.

For measurements, a laboratory photovoltaic absorptive nephelometer was used [5]. The basis of the device's operation is the principle of measuring the absorption or diffusion of light of the test medium. Measurement is performed using air filter No 2 with a wavelength of 500x10 nm. The analysis is carried out by determining the light transmission rate of dye solutions at different concentrations. Based on study indicators, we construct the calibration curves of optical density (D₀) dependence on dye concentration (C₀) for the initial solutions. Upon dye interaction with the crushed weighted amount of the semi-finished product, we determine the optical density of the dye solution (D), and according to the calibration curve ~ equilibrium concentration of dye in the solution (C). Based on data obtained we calculate dye adsorption [mmol/g] by semi-finished product using the formula (1):
3. Results and Discussion

Several studies have been conducted [5] to determine the basic properties of dye solutions, which showed: dye is resistant to hard water (5 points, maximum estimate), resistant to electrolytes is estimated at 5 points. Visual observations during this study showed an increase in the brightness of the green tint when exposed to the colorant of sodium carbonate solution (the concentration of sodium carbonate solution is 100 g/l). The dye is readily soluble in water at a temperature of 45 °C.

Adsorption isotherm analysis (Figure 2) indicates a significant increase in the adsorption level for samples treated with a modified dispersion of montmorillonite. Thus, at a concentration of 0.5 mmol/l in an equilibrium solution, the adsorption level is 0.0185 mmol/g for the control sample (1), 0.0215 mmol/g for experimental option (2). An increase in the sorption of the dye by the derma will help to reduce its concentration in the dueing solution.

![Figure 2](image-url)

**Figure 2.** Adsorption isotherm of anionic black dye by the structure of the semi-finished product: total (a) and within the concentration of 0-0.03 mmol/l (b)

In order to study the quality of velour leather, a semi-finished product was coloured, made according to traditional technology (control) and treated with modified montmorillonite dispersion. Colouring of velour samples was performed using anionic black dye with consumption rate of 4% of the mass of semi-finished product. Dye fixation in derma structure was performed with a solution of formic acid, consumption rate of 0.5% of the mass of semi-finished product. Dying time – 75 minutes, temperature – 50–55 °C. After the process of dying and conduct a rince, the samles was lubrication 40 minutes at temperature 65 °C. fat consumption – 7% from weight finished product.

Adsorption studies (figure 3) for non-lubrication specimens (1) and after lubrication (2) allowed detecting that level of adsorption for non-lubrication specimens was higher by almost 30%, with the
same index for samples after lubrication. This is probably due to shielding of the derm structural elements by components of fatliquoring emulsion.

![Figure 3. Adsorption isotherm of anionic black dye with structure of the semi-finished product before (1) and after (2) fatliquoring]

For all samples of colored velour defined complex properties [4], which characterizes mechanical properties of velour (Table 1) and the quality of color achieved (Table 2).

**Table 1. Mechanical properties of velour**

| Treatment options | Tensile strength at break [MPa] | The relative elongation at break [%] |
|-------------------|---------------------------------|-------------------------------------|
| 1 (control)       | 14.1                            | 39                                  |
| 2                 | 15.5                            | 32                                  |

**Table 2. Quality indicators of velour coloration**

| Treatment options | Sample colour      | Coloration resistance to dry friction, score | Coloration resistance to wet friction, score | Coloration resistance to organic solvents, score |
|-------------------|--------------------|---------------------------------------------|---------------------------------------------|-----------------------------------------------|
| 1 (control)       | black-green        | 4                                           | 2,5                                        | 2,5                                           |
| 2                 | black              | 5                                           | 4                                         | 5                                             |

The visual evaluation of samples showed the absence in samples treated with the modified dispersion of montmorillonite, a green tint in the resulting colour. The organoleptic evaluation showed that the samples of second group are more dense compared to samples of the control group. In this case, the samples treated with a dispersion are less dense, but not rigid. The conclusions of the organoleptic evaluation confirm the results of tests for mechanical parameters. Thus, the strength of the leather option 2 compared with the control one increased by 11%, and elongation decreased by 18%. The additional formation of derma is indicated by more uniform pile on samples of group 2 after repeated velour polishing. There is also a slight (3-4%) increase in thickness of the test samples after their dispersion treatment.

Quality tests of obtained colour showed an increase of 20% in resistance to dry friction of specimens filled with dispersion of montmorillonite. Significant difference (37.5%) is observed in parameters when determining the resistance of coloration to wet friction. The increase in these parameters indicates the formation of additional hydrogen bonds in the process of colouring. Double increase in resistance of test samples to organic solvents compared with the control group also
indicates the formation of additional bonds between the dye and derma. Hydrogen bonds formed in the system are destroyed by effect of organic solvent. Thus, most likely, we can talk about formation of covalent bonds, resistant to the specified type of processing. The formation of bonds of the aforementioned type may also indicate the disappearance of dye tint and obtaining deep black coloration in specimens of the second group.

4. Conclusions

Despite the fact, that the specific gravity of montmorillonite is large, different connections are formed between the active elements of the dermal collagen, dispersion and chemical materials. This formation is shown by an increase (by 11%) of samples strength with without the softness modification.

Projections confirmed for improved quality of velour coloration. This is shown by the improvement in each parameter that characterizes the quality of leather colour. Most likely, this is due to the fact that the montmorillonite modified dispersion has anionic nature, to fix which the sodium formate was used. The sodium formate in solution recharges the system of montmorillonite and transforms it into a cationic form. The dye used is anionic in its nature, and hence, there is a probability of establishing bonds between charged groups. This was confirmed based on study results through increase in adsorption of dyes by derma, an increase in resistance of the obtained coloration to mechanical effects and organic solvents.

When implementing the technology of velour colouring the leather enterprise uses auxiliary substances for due diffusion in derma structure. Often, these are surface-active substances that reduce velour and its products resistance to water in general. The use of montmorillonite modified dispersion allows excluding these substances from the process. Treatment with the montmorillonite dispersion arranges the porous structure at the level of fibrils and primary fibers [1]. At the same time, the thickness of collagen fibers increases, derma structure adhesiveness decreases sharply and dye diffusion improves. Complete coloration of derma with dye was achieved during this study within 30 minutes of treatment.

Consequently, application of montmorillonite modified dispersion in velour production contributes to an increase in both leather colour quality and its quality as a whole.

References

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