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Fatliquoring agent and drying temperature effects on leather properties

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Leather, a collagen structure material, usually requires the addition of fatliquoring agents that have been recently found to cause instability during heating in critical manufacturing processes. The effect of fatliquoring agent concentration and drying temperature on the leather properties was investigated. Leather shrinkage, leather absorption of water and water vapour, and water vapour permeability were measured under defined conditions. The samples of bovine leather obtained after commercial liming and chrome tanning processes were used. The samples were fatliquored with 3, 6, 9 and 12% solutions of anionic synthetic fatliquoring agent and dried at different temperatures. The results of the investigation are corroborated by scanning electron microscope (SEM) study. It was shown how the concentration of fatliquoring agent and drying temperatures influence the leather properties.

1. Introduction

Collagen, an amphoteric fibrous protein, is present in animal skins and hides as a porous matrix along with some noncollagenous matter. In leather processing hides are first purified to remove noncollagenous matter in pretanning operations; liming, deliming and pickling. The purified (pickled) matrix is tanned by treatment with aqueous solutions of basic chromium sulphate, fat liquored, dyed and dried to obtain leather [1]. Fig. 1 shows a typical scheme for leather processing. Chrome tanned leather has many favourable properties such as softness, flexibility, strength, durability and hydrothermal resistance [2].

Most domestic leather is of type that requires the addition of special softening oils called "fatliquors". These are sulphated oils, treated with sulphuric acid so that they will react with the molecules in the leather. Flexibility requires the leather fibers to be separated from each other. Fat prevents the sticking, glueing or adhesion of fibers [3]. In the wet state, the leather is fully lubricated by the water which is held between the fibre bundles and between smaller fibrils. It can be flexed, stretched, deformed or moulded into almost any shape. As the water is removed, however, the fibres approach each other and can stick together to a greater or lesser extent, giving a range of possibility flexibilities depending on the rate and manner of the moisture removal. The method of drying has to be adapted to the characteristics required of the leather. The perfect method of drying is that which yields the required leather in the largest area or volume [4].

The development of leather softness first originates in the beamhouse with the chemical opening up of the collagen fibres. To retain the open fibre structure and tendency towards softness originally imparted by chemical processing, it is important to ensure adequate lubrication of the fine fibrils as well as of the coarser fibril bundles/fibres. This is achieved by the use of fatliquor emulsions of small particle size capable of penetrating down the hierarchy of the leather structure. This, in conjunction with the use of relatively mild drying conditions minimizes the extent of fibril, as well as fibre, readhesion during drying process. This promotes leather softness and reduces the need for subsequent stress softening. The current view of the changes in ultra-structure that occur during drying is that the diameter of collagen fibrils shrink during drying and the cracking of the fatliquor emulsion allows the neutral fraction to lubricate the fibril and prevent sticking during drying process [5].

This study is concerned with the changes that occur when collagen is heated to temperatures exceeding the shrinkage temperature (T_s). During the first stage of heating it loses the bound water. This is followed by a thermal decomposition (pyrolysis) of the sample. Among the known tanning agents only chrome salts may increase T_s over 100°C [2].

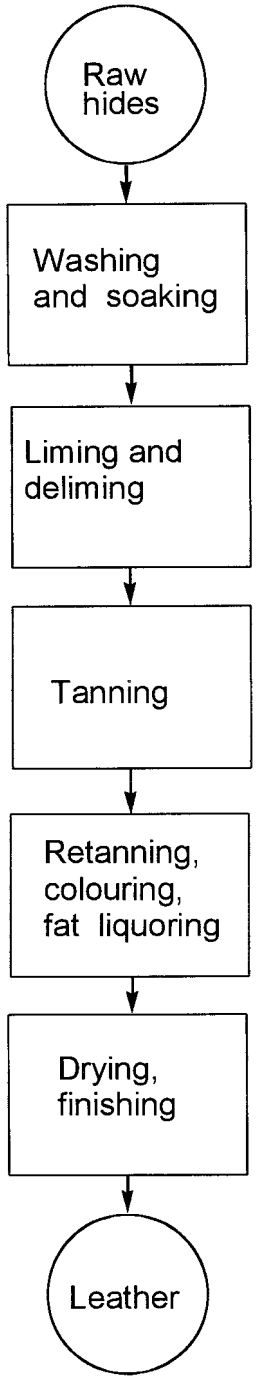


Figure 1 Scheme for leather processing.

2. Experimental procedure

2.1. Materials

In this study, raw bovine hide (the weight category of 35 kg) is used. All the hide samples were from the dorsal region. Thus, heterogenous leather structures from other regions were avoided. The hide had been limed with 1.2% sodium sulphide, 1.5% sodium hydrosulphide and 3% calcium hydroxide. Deliming was performed with 1.5% ammonium sulphate. Acidification was carried out using 6% solution of industrial salt (solid NaCl), 0.9% solution of formic acid and 0.4% solution of sulphuric acid. The samples were taken from the processed leather which had been tanned with 7% solution of basic chromium (III) sulphate (containing ca. 26% Cr_2O_3 of basicity 33%) which corresponds to 1.25–2.50% Cr_2O_3 per kg of leather. The dried samples contained 16% of moisture.

The samples were fatliquored with 3, 6, 9 and 12% solutions of anionic synthetic fat liquoring agent having 35% of active substance. Synthetic sulphated spermaceti oil product with long chain esters was used as the fat liquoring agent. Corresponding samples which were not fatliquored were examined as well.

The samples were dried at temperatures of 60, 90, 120 and 150°C. The drying process was carried out in a dryer for 2 hours. Afterwards, shrinkage of the leather, leather absorption of water and water-vapour, and water-vapour permeability were determined.

2.2. Leather properties measurement

The International Union Physical (IUP) methods [6] were applied for measuring water vapour permeability of leather, leather absorption of water and water-vapour. Leather shrinkage (% area change) was determined after drying for 2 hours. The percentage of leather shrinkage, D_A, was determined according to Equation 1:

$$D_A = (A_1 - A_2) * A_1^{-1} * 100 \quad (1)$$

A_1 and A_2 are the areas of the leather sample before and after drying, respectively. Herfeld apparatus (shown in Fig. 2) was used for determining water vapour permeability (using DIN 53333 (IUP 15) method) and leather absorption of water-vapour. The leather sample was clamped across the mouth of a glass bottle which contained 50 ml of water. The bottle was kept in a desiccator containing 97% H_2SO_4. The bottle was weighed periodically to determine the mass of vapour transmitted through the leather and absorbed by 97% H_2SO_4.

Water vapour permeability (WVP) was determined according to Equation 2:

$$\mathrm{WVP} = (m_2 - m_3)^{-1} * S * t \quad (2)$$

where m_2 is mass of apparatus containing leather sample and 50 ml of water before measurement, m_3 is mass of apparatus containing leather sample and water after keeping in a desiccator during 8 hours, S is surface

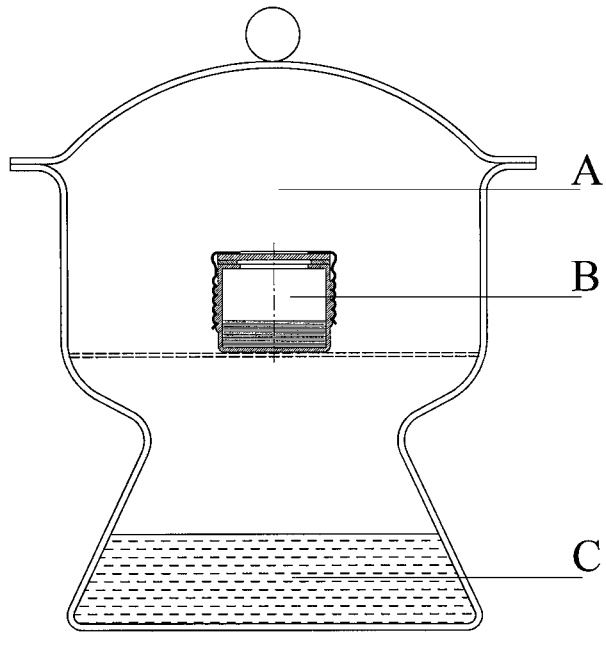


Figure 2 Herfeld apparatus.

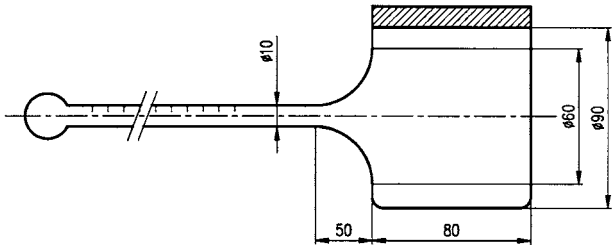


Figure 3 Kubelka apparatus.

of leather sample, and t is measuring time interval in hours. Absorption of water-vapour (AWV) was determined according to equation 3:

$$\mathrm{AWV} = (m_4 - m_1) * S^{-1} \tag{3}$$

where m_1 is mass of leather sample before measurement, m_4 is mass of leather sample after the process was completed, and S is surface of leather sample.

Kubelka apparatus (using DIN 53330 (IUP 7) method) and Bally penetrometer type 5162 (using DIN 53338 (IUP 10) method) were used for determining the absorption of water. The Kubelka apparatus was made of glass and had the dimensions shown in Fig. 3. It is designed to measure the water absorption by static method in which the leather sample is immersed into 100 ml of water (determined by a graduated glass tube). After period of 2 hours a volume of the absorbed water is evaluated.

The water absorption, P, in ml of water per 100 ml of leather, was determined as a product of the absorbed water and the leather sample volumes. The water absorption, Q, in ml of water per 100 g of leather was determined as a product of the absorbed water volumes and the leather sample mass.

Dynamic waterproof mass tests were performing using a Bally penetrometer. The percentage of water absorption, WA, was determined as a product of mass of leather sample before measurement and the difference between mass of cylinders with leather sample after and before testing, respectively.

2.3. Scanning electron microscopy (SEM)

Electron micrographs of leather samples were taken using a Cambridge Stereoscan 600 scanning electron microscope (SEM). Samples were coated with gold 10–20 nm thickness using an Edwards S 150 Sputter Coater. Cross section examined of all the leather samples was corium layer.

3. Results and discussion

3.1. Leather properties determination

The drying temperatures used were 60, 90, 120 and 150°C, and values (in percentage) for evaporated

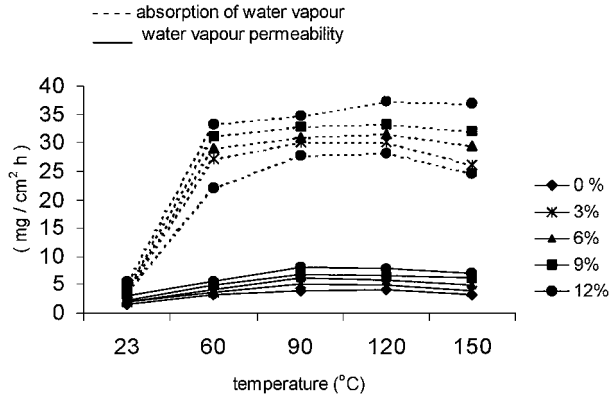


Figure 5 Absorption of water-vapour (dashed lines) vs. drying temperature and water vapour permeability (solid lines) vs. drying temperature at different percentages of fatliquoring agent.

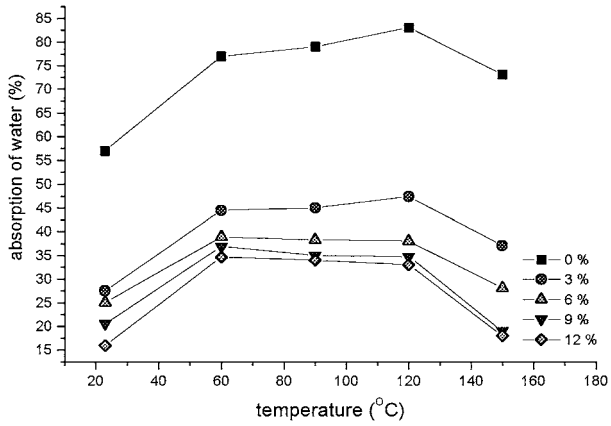


Figure 6 The dependence of leather absorption of water (measured by Kubelka apparatus) on different drying temperatures at different percentages of fatliquoring agent.

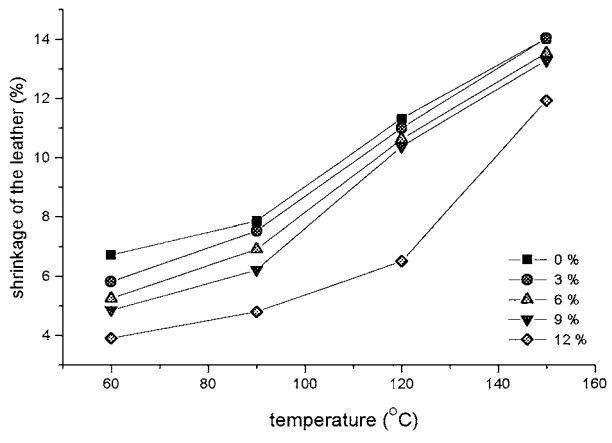


Figure 4 The dependence of leather shrinkage on different drying temperatures at different percentages of fatliquoring agent.

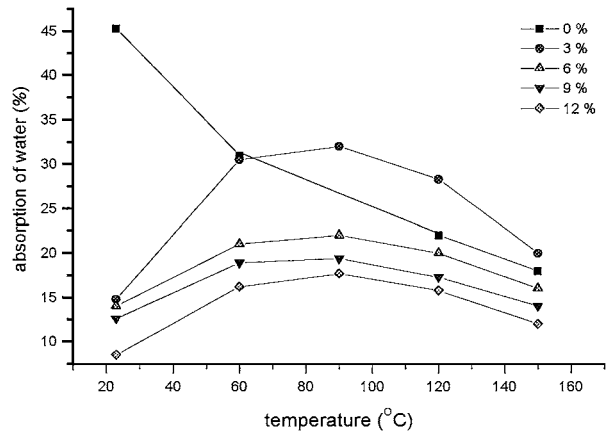
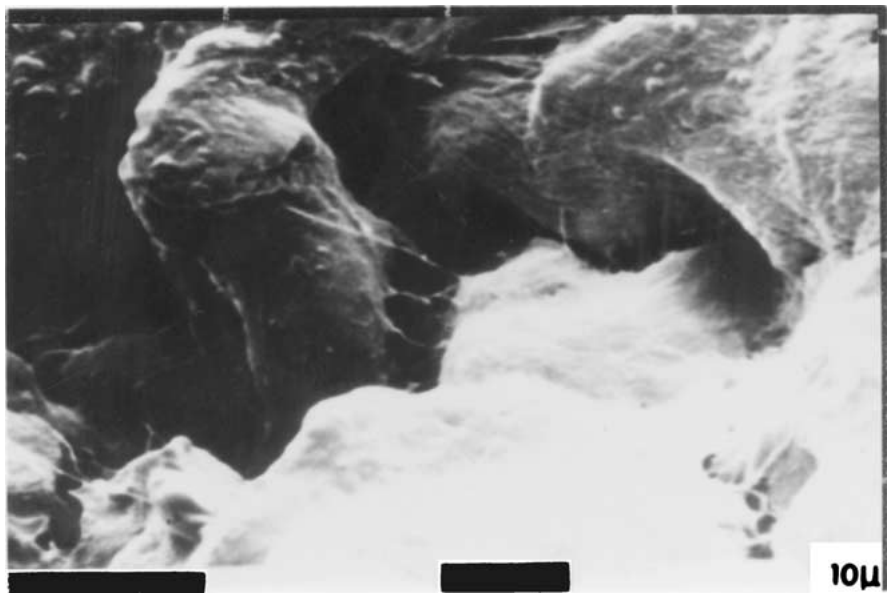
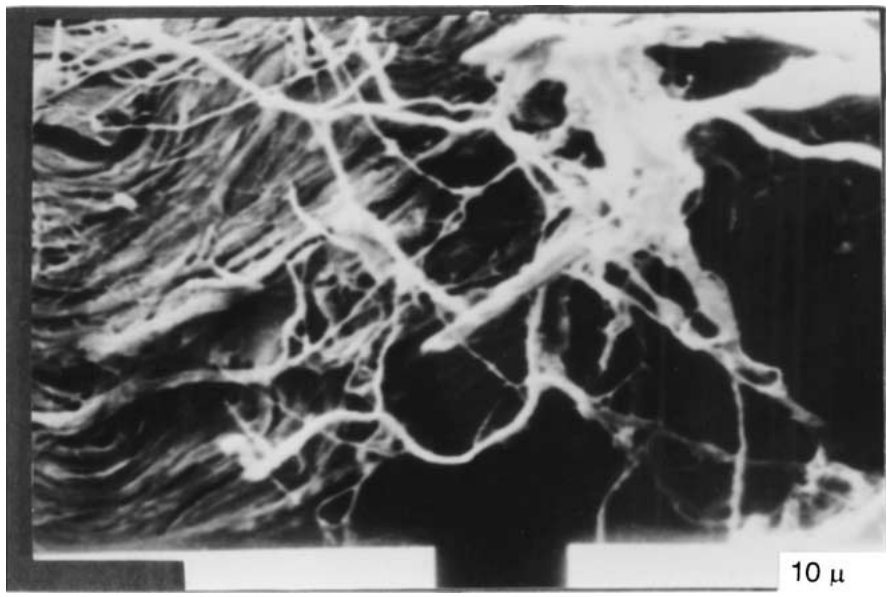


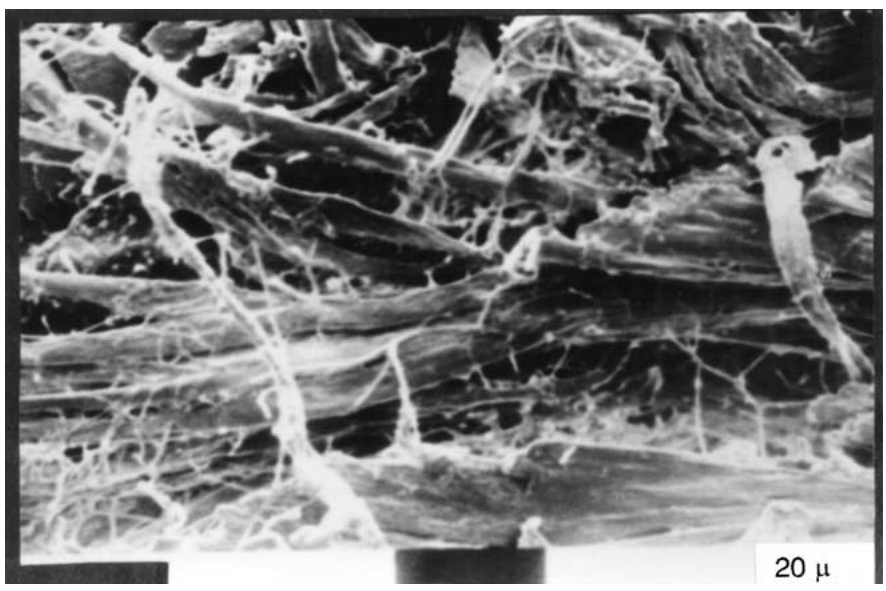
Figure 7 The dependence of absorption of water (measured by Bally penetrometer) on different drying temperatures at different percentages of fatliquoring agent.



(a)



(b)



(c)

Figure 8 SEM photomicrographs of (a) raw hide sample, (b) chrome tanned leather sample, (c) processed leather sample liquoring with 9% solution of fatliqouring agent.

moisture, during a drying process of 120 minutes, were 8.55, 12.87, 15.26 and 16.65, respectively. It was of a special interest to examine effect of temperatures higher than 100°C on leather properties. Higher temperatures are applied in some processes of shoe manufacture. Higher temperatures are also important parameters in fireproof shoe and clothes manufacture. Higher temperatures may subject the leather to damaging heat treatments such as wet heat processes used for stress relaxation and dry heat processes, of up to 120–130°C, used to set the shoe to the required shape. The sole and heel attachment may be equally damaging to the leather because it may involve even higher temperatures (up to 170°C), depending on whether cementing, vulcanizing, or injection molding is used [7]. The results are reported in Figs 4–8.

Fig. 4 shows the result for leather shrinkage at different temperatures. The percentage of leather shrinkage increased progressively with increase of drying temperature. The percentage of leather shrinkage was higher in leather samples fatliquored with lower percentage of fatliquoring agent (shown in Fig. 4).

The results for leather absorption of water-vapour and water vapour permeability are shown in Fig. 5.

Fig. 6 gives the results for absorption of water measured by Kubelka apparatus and on the Fig. 7 results for absorption of water measured by Bally penetrometer are shown. Both of these measurements were carried out after the absorption during 120 minutes.

Permeability deriving from specific fibrous structure of leather is important property of processed leather [8]. As a result of the fibrous structure, there are natural voids in leather. The most of volume of water-vapours and gases deriving from perspiration of the body evaporate through pores [9]. Permeability of collagen matrix in the leather is very high (50–90%), depending upon the type of animal and region of the skin. Permeability of a material is determined with number of pores (voids) on the determined area. Voids are of a size ranging from about 0.5 μm to 5 μm in all samples. Only a few studies on diffusion in collagen matrix were reported [10].

In our study, the absorption of water-vapour and water vapour permeability increased with the increase of drying temperature. This increase was observed up to temperature of 120°C, whereupon values begun to decrease. As a result, larger deviation of values was found above temperature of 120°C. It was reported that melting process of leather started at temperature above 120°C [7].

In all experiments, the absorption of water-vapour and water vapour permeability were higher in the case of less fatliquored leather samples. The fatliquoring agent is dispersed among collagen fibers in leather matrix resulting in decrease of the void volume and in reducing of water diffusion. It was found that fatliquor binds to particular sites on the collagen molecules as a droplet. Each droplet contains only few molecules that are in contact with the collagen, the rest being excess material that can destabilize it [11]. Significant increase of the water vapour permeability was observed at temperature between 23 and 60°C.

All of the measurements made on Kubleka apparatus are shown on Fig. 7. The most of water absorption was observed in non fatliquored sample. The absorption of water increased with the increase of drying temperature up to 120°C. As expected, the absorption of water decreased with the increase of concentration of fatliquoring agent. This implies that the increase of fatliquoring agent concentration causes an increase in hydrophobicity of collagen matrix of the leather.

The absorption of water, measured on Bally penetrometer (Fig. 8), also increased with the increase of drying temperature up to 120°C and decreased with the increase of concentration of fatliquoring agent. However, the absorption of water of non fatliquored sample (measured on Bally penetrometer) decreased rapidly with the increase of drying temperature up to 60°C and more slowly from 60°C to 150°C. At the room temperature the absorption of water is much higher in non fatliquored sample. This sample is more hydrophilic due to the absence of fatliqouring agent. However, the volume of voids in its collagen matrix is reduced with the increase of temperature resulting in decrease of absorption of water in non fatliquored sample.

3.2. The structure of voids and fibers in collagen matrix of leather samples

SEM photographs are presented in Fig. 8a–c. Fig. 8a gives SEM photograph of raw hide sample, Fig. 8b SEM photograph of chrome tanned leather sample, and Fig. 8c SEM photograph of processed leather sample liquoring with 9% solution of fatliquoring agent. SEM photographs (shown in Figs 8a–c) show the structure of voids and fibers in collagen matrix of three different leather samples. In the case of raw leather (Fig. 8a), fibers have thickness of *ca.* 16 μm in section and are connected with transversal fibrils of 0.3 μm. After chrome tanning process fibers in leather matrix (Fig. 8b) have more defined sections. The fibers are detached and have thickness of ca. 6 μm. Chrome tanned leather sample after treatment with 9% of fat liquoring agent (Fig. 8c) is even more compact than both of previously mentioned samples. The voids have averaged diameter of ca. 5–6 μm in all samples.

4. Conclusion

Data on leather shrinkage were obtained from chrome tanned leather samples after treatment with 0, 3, 6, 9 and 12% solutions of fatliquoring agent, respectively. The examined properties of leather depend on drying temperature and percentage of fatliquoring agent. The leather shrinkage increased with increase of drying temperature and was reduced in the case of more fatliquored leather samples.

The water vapour permeability of leather, leather porosity of water-vapour and leather absorption of water (measured on both Kubelka apparatus and Bally penetrometer) increased, in principle, with the increase of drying temperature up to 120°C.

The data indicate that particular leather properties depends on change in volume of water, dispersed in collagen matrix, which evaporates during drying process

at temperatures up to 120°C. The melting process of leather usually occurs at about 120°C, where upon change of fibers structure and leather permeability are enhanced [7].

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