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Parametres of Fountain Pen Ink Using Common Alder (*Alnus glutinosa* L. gaertn) Leaves by Fermentation Method

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Formation of gallic acid from common alder (*Alnus glutinosa* L. gaertn) leaves has been carried out by fermentation method. $FeSO_4$ was added to form black complex used as fountain pen ink after addition of gum to adjust the viscosity of the ink. Some physical parameters of the common alder ink such as viscosity, density, drying time and pH were investigated and these properties were compared with two commercial inks.

Key Words: Fountain pen ink, Iron gall ink, Gallic acid, Gallotannate complex, Common alder (*Alnus glutinosa* L. gaertn).

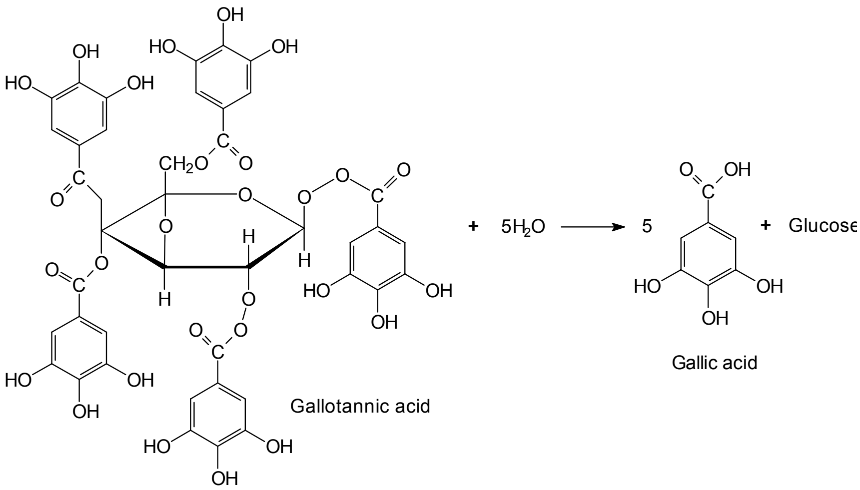
INTRODUCTION

Iron-gall ink is the most common ink that used before the nineteenth century, both for writing and drawing. It was the mixture of iron(II) sulphate, gallic acid and gum[1].

There are various formulations for ink preparation. They share common ingredients such as gallic acid molecules and Fe^{2+} ions. Iron gall ink is formed by the reaction between tannic acid and $FeSO_4$. The active components of tannin are gallotannic and gallic acid[1] (**Scheme-I**).

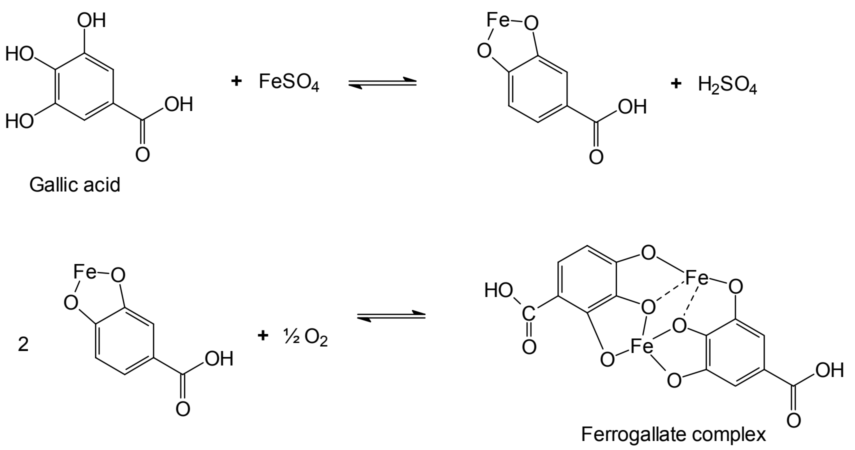
Gallotannic acid is the mixture of glucose esters which on hydrolysis yielded gallic acid and glucose during preparation of ink.

Krekel studied the reaction between $FeSO_4$ and gallic acid. In this reaction first gallic acid reacts with $FeSO_4$ to form ferrogallate which is colourless and soluble in water. Ferrogallate oxidizes by the air oxygen and finally ferric pyrogallate complex is formed which has purple-black colour. Water molecules fill the unsettled places to complete the octahedral structure of the iron complex[2]. Small amount of the pigment may be formed by the reaction of the oxygen in water and the pigment. But, much of the pigment is formed when the ink is applied to the paper surface and allowed to exposure for several days[3].



Scheme-I

There are three methods for the extraction of gallic acid from the plant. First method is extraction of gallic acid by letting the plant in deionized water or another liquid at constant temperature. Second, heating the plant at its boiling point and the last, heating the plant at its boiling point and then let to fermentation. The most bright and intensive ink is formed by fermentation method. When mould softened the gallotannic acid with the help of heat enzymetically, the solution is converted to gallic acid. A black coloured complex is obtained by the reaction of gallic acid and $FeSO_4$. The reaction can be written as follow[2] (**Scheme-II**).



Scheme-II

In this study, the optimum experimental conditions were carried out for forming the fountain pen ink using the extract of common alder (*Alnus glutinosa* L. gaertn), $FeSO_4$ and gum. The physical parameters were compared with two commercial inks.

EXPERIMENTAL

$FeSO_4$ was supplied from Merck and gum was purchased from stationery. Infrared spectras of the ink samples were taken as KBr disk a Jasco FT/IR 430 model spectrometer. The pH values of the samples were determined by a WTW Multiline P3 pH/LF model pH meter. Viscosity were determined by Ostwald viscosimeter. Drying oven M 5040 P model was used for stabilization of fermentation temperature.

Common alder (*Alnus glutinosa* L. gaertn) leaves were collected in Tokat (Turkey) in June, 2005. After collection, the leaves were dried at room temperature, powdered and stored under suitable conditions.

Extraction of common alder (*Alnus glutinosa* L. gaertn): Dried and powdered plant material (25 g) was extracted using soxhlet apparatus in 300 mL of deionized water for 0.5 h at 90 °C and concentrated to ratio of 4/5 (v/v).

Determination of fermentation period related to temperature: The solution extracted from *Alnus glutinosa* L. gaertn was concentrated to the ratio of 4/5 due to increase the intensity of the extract. Laboratory oven was adjusted at various temperatures (21, 22, 23, 24, 25, 26 °C), separately and the solutions were allowed to fermentation. The pH values of the environment was measured every 24 h.

Determination of $FeSO_4$ amount: The concentrated solution fermented at 21 °C for 8 d was used and $FeSO_4$ was added to 5 mL of this solution increasing amount of 0.05 g starting from 0.1 to 1.05 g.

Determination of gum amount: The amount of gum was determined according to the colour intensity as qualitatively. Different amounts of gum was used for the same solution that mentioned above and optimum value was determined.

Measurement of physical parameters of iron gall ink and the two commercial inks

Measurement of ink density: The unknown density of the iron gall ink was evaluated with picnometer. The experiments were carried out at room temperature (25 °C) and this processes were repeated for the two commercial inks.

Measurement of viscosity: The inks' viscosity determinations were performed using an Ostwald viscosimeter. 100 mL of the each samples were placed into the viscosimeter and time of flow of a specific volume through the capillary was measured at various temperatures (20, 25, 30 and 40 °C) for each sample, separately. Distilled water was used as reference for viscosity. Calculations were estimated using the eqn. 1 which is derived from Poiseuille equation.

$$\frac{\eta}{\eta_0} = \frac{\rho t}{\rho_0\ t_0} \qquad (1)$$

here, η_0 and η are viscosity coefficients of the reference liquid and of the experimental liquid, respectively. t and t_0 are flowing times of the reference compound and liquid in the capillary tube which has ν volume with l length and r radius, ρ and ρ_0 are the densities of the experimental liquid and reference compound, respectively.

Viscosity values were determined according to eqn. 1 at various temperatures for three types of inks (Fig. 1).

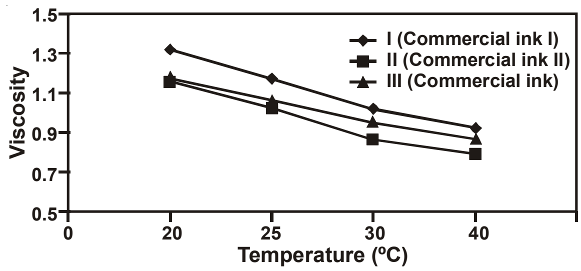


Fig. 1. Viscosities of the ink samples at different temperatures

RESULTS AND DISCUSSION

In present work, fountain pen ink was made with common alder (*Alnus glutinosa* L. gaertn) leaves using $FeSO_4$ and gum by fermentation method. The fermentation period was determined according to pH variation.

The fermentation periods can be determined from the Fig. 2 according to the minimum values of the curves. It means that pH values increases after the concave. However, acidic substance amount such as gallic acid decreases. In addition, it is observed that colour intensity is proportional with the fermentation period. Consequently, optimum temperature and fermentation period was found as 21 °C and 8 d, respectively.

The most important subject on iron gall ink is the corrosive character of these inks. Because of this reason, it damages the paper after penetration of the ink and it forms hole on the surface. The most important reason for this damage was the excessive Fe^{2+} amount[4] so, the concentration of Fe^{2+} has a big importance. The efficient amount of $FeSO_4$ was observed as 0.75 g. This can be due to the excessive Fe^{2+} ions which doesn't accompany the formation of ferric pyrogallate complex and form another complex

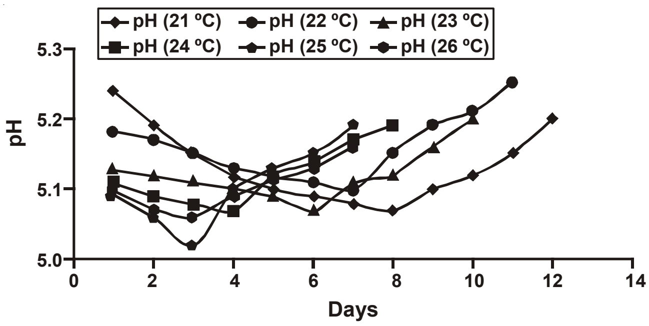


Fig. 2. Effect of fermentation period related to pH variation at different temperatures

structure with other molecules that present in the medium. However, excessive $FeSO_4$ amount causes corrosive damage of paper and formation of residue on the bottom of the flask. The amount of $FeSO_4$ have high importance in making iron gall ink because of these reasons.

The amount of gum has a great importance due to the good penetration to the paper surface and optimum viscosity value. However, excessive amount of gum causes fading in the colour of the ink. On the other hand, inadequate gum amount doesn't allow good penetration of the ink to the paper surface. At the end of the investigation the optimum amount of gum was determined as 0.7 g for 5 mL of the solution.

It can be clearly observed from Fig. 1 that there is no considerable difference in viscosity values for the ink samples. The viscosity values of common alder ink were very close with the commercial ink (II).

The densities of commercial ink (I), (II) and common alder ink were determined as 0.892, 1.012 and 1.063 at 26°C, respectively. As can be seen from these values, not only the common alder ink has the close viscosity value but also close density with the commercial ink (II).

At last, pH values and drying times of the ink samples were measured (Table-1). pH value of commercial ink (I) is near to neutral value (pH 6.70). However, the others are exhibit strong acidic properties. Thus, both the pH value (1.45) and drying time (100 s) of the common alder ink is similar with the commercial ink (II).

TABLE-1
DRYING TIMES AND pH VALUES OF INK THE SAMPLES AT ROOM TEMPERATURE

	Drying time (s)	pH
Commercial ink (I)	70	6.70
Commercial ink (II)	90	2.82
Common alder ink	100	1.45

According to the IR spectra of the ink samples, in the functional group region, the signals fit each other and wavenumber of some groups of the samples are seem similar in the fingerprint region. Commercial ink (I); IR ν (cm^{-1}) : 3442 (O-H stretch), 2381, 2078 (CO_2 adsorbed from atmosphere), 1637 (C=O stretching), 1398, 1099, 566, 526, 484, 474, 443, 424, 414, 401; Commercial ink (II); IR ν (cm^{-1}) : 3457 (O-H stretch), 2381, 2076 (CO_2 adsorbed from atmosphere), 1637 (C=O stretching), 1498, 1392, 1186, 1122, 1033, 1006, 605, 557, 528, 468, 445, 428, 416, 408; Common alder ink; IR ν (cm^{-1}) : 3417 (O-H stretch), 2061 (CO_2 adsorbed from atmosphere), 1635 (C=O stretching), 1417, 1106, 574, 497, 462, 437, 424, 412. In the IR spectra of the three ink samples, characteristic peaks for OH groups were observed as broad signals between 3690-2500 cm^{-1}. The broadening of this peak shows that these inks have strong intramolecular hydrogen bonding between the hydroxyl group of the gallic acid and water molecules.

The results show that it is possible to make fountain pen ink using common alder (*Alnus glutinosa* L. gaertn) leaves. Generally the physical parameters of common alder ink were found proximate with the other two commercial inks. Consequently, if the common alder leaves is used in ink industry, it will probably be an important raw material for commercial use. Further investigations are going on.

ACKNOWLEDGEMENT

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