THE USE OF IRON NANOPOWDER IN DACTYLOGRAPHY

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Abstract

The article is focused on the solution of a very urgent problem associated with the diagnostics and prognostication of functional properties of magnetic dactylographic powder. The iron-containing powder is studied. The samples of this powder are obtained using the conductor electric burst. This powder is also investigated using transmission electron microscopy (TEM), X-ray diffraction analysis (XRDA) and hydraulic absorption (pH - measurement). It was shown, that passivation of metallic iron in oxidizing medium forms an oxide film around the iron core. The passivation conditions affect the composition and structure of this oxide film. A new parameter was found, namely, the rate of change of pH aqueous suspension with time characterizing the oxide film adhesiveness. This parameter reflects the hydrophilic / hydrophobic behavior of oxide compounds and can be used for prognostication of functional properties of magnetic dactylographic powder.

Keywords: Nanopowder, iron, hydrolytic adsorption

INTRODUCTION

The fingerprint expert use fine-dispersed powder-dyes to develop the colorless sweat and grease deposits (footprints). The mainly used powder is dry-powder developers [1-2]. They consists either of partially oxidized metallic iron (for its pyrophorosity decrease) or of a metallic iron and ferrioxide pigment mixuture. At present, the problem to equip the criminalistics laborotories with domestic dry-powder developers is very urgent.

Dactylographic informativeness of a fingerprint of a sweat and grease deposit (print) is defined not only by the pigment granule size, but also by its adhesive and adsorptive properties. Sweat and grease fingerprint consists of water, grease component and salts. According to the adhesion theory [3] hydrophobic powder should demonstrate good development of 'old' (dry) fingerprints on the wetted footprint-carrying surfaces. Hydrophilic powder demonstrates good development of "fresh" (wetted) footprints on dry footprint-carrying surfaces.

The purpose of this work is to find out the interconnection of nano-sized iron powder with the development quality of a sweat and grease footprint.

1. THE OBJECTS OF RESEARCH AND RESEARCH TECHNIQUES

Nano-sized iron powder is obtained using conductor electric burst at high pressure in an inert medium (iron of conductor electric burst). To decrease iron pyrophorosity its passivation in an oxidizing medium was conducted. The passivation conditions are different [5-6]. Specimen № 1 was passivated at 20°C with additional heating in a muffle furnace (slow temperature rise from 20°C to 180°C during 35 hours).

The composition and structure of the oxide film on the iron core were studied using X-ray diffraction analysis on the diffractometer "Difray-401" and transmission electron microscopy (TEM) on TPU Nano-Center equipment ("JEOL JEM - 2100F" device).

The wetting properties of powder were studied using hydrolytic adsorption. The kinetic version of pH-measurement control was used [7]. The suspension was prepared in the following ratio: "water: powder =50". The initial water acidity was 6.7÷6.9 units of pH. The pH variations of aqueous suspension with time were

registered by pH-150M (measurement accuracy - ± 0.03 units of pH) in every 5 seconds of contact. Aqueous suspension was continuously stirred by a magnetic stirrer. From the obtained data the rate of pH-suspension change was estimated ($U_{pH} = \Delta pH_i / \Delta\tau, \min$). This value was accepted as a parameter of "wetting rate" [8-9].

Dry and bright (light) surfaces of paper, glass and polyethylene film were chosen as fingerprint-carrying surfaces.

2. RESULTS AND DISCUSSIONS

2.1. The results of transmission electron microscopy and X-ray diffraction analysis

Transmission electron microscopy analysis has shown that the average size of powder particles is within the same nano-sized range (100÷200 nm). The samples passivated in different conditions have some differences in the composition and structure of their oxide layer.

The oxide layer thickness for specimen № 1 (**Figure 1**, photo 1 „a") is uniform and equals 0.269 nm. The lines of atoms are solid and have one direction. The distance between the lines of atoms is 0.269 nm. It corresponds to the maximal reflex on its intensity with d(104)=0.269 nm, which is typical for ferric oxide with a hematite structure (α-Fe_2O_3).

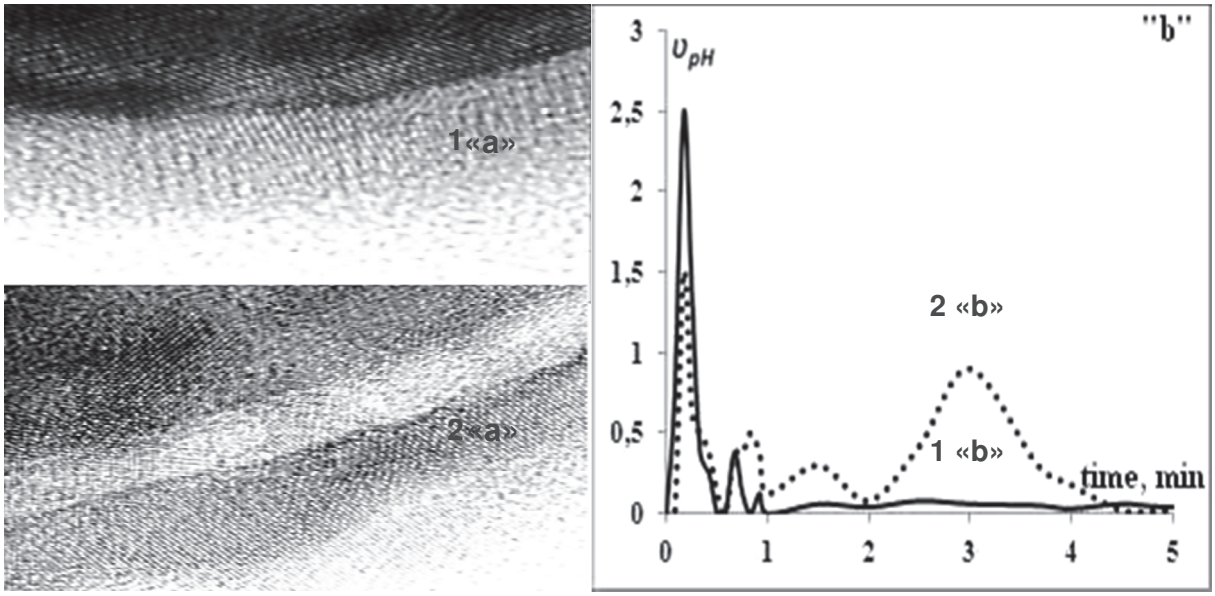


Figure1 Transmission electron microscopy - figure («a») and kinetic curves of wetting rate - figure («b»): 1) - specimen 1, 2) - specimen 2

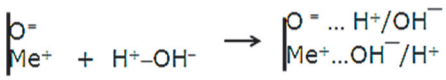
There is a two-layer oxide coating in the specimen 2 (**Figure 1**, photo 2«a») (its thickness is 20 nm). The oxide layers have the same thickness (10 nm), but differ in packing color and density: the external layer is denser and darker than the inner one. It is obvious, that the oxidation of the specimen 2 was in nonequilibrium conditions. Those conditions are provided by the different rates of counter diffusion flows of oxigen and iron ions. The oxigen supply is complicated by the presence of a formed hematite film. The flow of iron ions from inside is facilitated by the temperature rise. The isostructural iron oxides with a defective spinel structure of maghemite (γ-Fe_2O_3) and magnetite types (Fe_3O_4) are formed in such condiotions [10-12]. These oxides differ in the parameters of light deflection, the density of granules (grain) packing, the temperature of formation and adhesion to iron core. Magnetite is fomed at higher temperature, posesses better adhesion and is darker and denser (n=2.42 and density ≈$5.3 \cdot 10^3$) than maghemite. (n>2.52 and density ≈ $4.9 \cdot 10^3$). This data gives

evidence, that the external layer is represented by magnetite granules, while inner layer is represented by maghemite granules [13-14].

The results of X-ray diffraction analysis confirm the conclusions made on the basis of transmission electron microscopy analysis. There are only four reflexes typical for iron in the specimen 1. Four iron reflexes and five reflexes typical for both maghemite and magnetite have been discovered in the specimen 2 [15]. It can be explained by the similarity of maghemite and magnetite crystal structures, high dispersion and low rate of crystallinity of nucleus of oxide structure [16].

2.2. Research results using hydrolytic adsorption technique

When there is a contact of solid with water the reaction zone is not on the whole surface, but only in some special points (active acid-base surface centers). Therefore, the acid-base interaction depends on the nature, force and concentration of active canters and is predetermined initially by the solid biography [17]. The results of pH-measurement research have shown, that the reaction of acid-base interaction of surface centers with water progresses on the following scheme:



The acidity change (acidification or alkalization) of suspension per time unit allows calculating the rate of pH suspension change ($\upsilon_{pH} = \Delta pH_i / \Delta\tau, \min$). This value is accepted as a parameter of "wetting rate".

It was found, that by the contact of solid with water the wetting rate changes with time. The rate acceleration and decrease for various samples is different (**Figure 1b**). For the specimen 1 surface wetting stops in one minute contact. The oxide film from hematite causes this process (α-Fe_2O_3). The octahedral iron ion environment by oxigen [18] forms active centres of basic nature (primary Lewis centres and secondary Brondsted centers): O^{2-} …H^+/OH^- . The surface OH^- - groups interconnected by hydrogen bonds shield the surface and prevent further diffusion of water molecules inside the oxide granule. It determines the surface hydrophobic properties.

The surface wetting for the specimen 2 is slower and longer (till 5 minute contact). The decrease of wetting rate is discrete. The oxide film from spinel-shaped oxides initiates this process. These oxides contain iron atoms in two different states $Fe^{3+}[Fe^{2+}Fe^{3+}]0_4$. Cations Fe^{2+} or Fe^{3+} are active centres being in tetrahedral arrangement on oxigen [19-20]. The unsaturation on oxigen forms the primary and secondary centers of acid nature Fe^{2+}… OH^-/H^+. In this case there is no two-dimensional hydrogen-bond net between canters and there is no resistance to wetting. The wetting process travels deep inside the friable oxide film and its rate changes discretely. The volumetric fill of adsorbent porous space by adsorbate solution determines the hydrophilic surface properties [21].

2.3. The results of dactylographic research

The sweat and grease fingerprint was covered by the pigments under study using a magnetic applicator. Dry and light surfaces of paper, glass and polyethylene film were choses as print-carying surfaces.

Dactylographic research has shown by fingerprinting the sweat and grease fingerprint using magnetic brush it is necessary to consider both adhesive and magnetic properties of the pigment (measured capture and light dropping of the pigment from the brush „pile"). The tested samples meet the demands of modern dactylography.

The specimen 1 has hydrophobic properties and, therefore, it does not form any clods by its long-term storage. It has good adherence to the sweat and grease substance of the print of different periods of prescription since the grease (fatty) component of the print is more stable. Due to low quantity of hematite the print of the sweat

and grease fingerprint has faded-grey color. The color contrast between the print and background is weak. The print is visually almost not clear. However, when a magnifying glass is used the cristae cutis are clear and visible. The magnetic susceptibility of hematite is low, therefore, the pigment is weakly retained on the the brush „pile“.

The specimen 2 also meets the requirements of dactylography. It has hydrophilic properties, therefore, its adhesive property is high only to fresh sweat and grease fingerprint (water-bearing). The prints are very clear and have distinctive golden coloration. They are visually clear on the background surface. The magnetic susceptibility of magnetite is high, therefore, the pigment is well retained on the brush „pile“.

3. CONCLUSION

1) Performance specifications of dactylographic magnet powders are determined not only by their physical parameters (the size of pigment particles), but also their chemical nature.

2) Ferrioxide compounds of different compositions and structure show different properties to surface wetting (hydrophilic and hydrophobic behavior) and interaction with fingerprint forming substance.

3) By the variations of passivation conditions of conductor electric burst we can achieve the optimal ratio of physical-chemical parameters of the pigment which results in the quality improvement of “developing” properties in dactylography.

ACKNOWLEDGEMENTS

We show appreciation to Professor Ilin A.P.

REFERENCES

[1] BELKIN, R. S. *Kriminalistika - problemy segodnyashnego dnya.* Moscow: NORMA-INFRA, 2001. 240 p.

[2] ISHCHENKO, E. P., TOPORKOV, A. A. *Kriminalistika: Uchebnik. Izdanie 2-e, ispravlennoe i dopolnenno.* Moscow: Infra-M, 2005. 748 p.

[3] FROLOV, Yu. G. *Kurs kolloidnoi khimii. Poverkhnostnye yavleniya i dispersnye sistemy.* - Moscow: OOO TND «Al'yans», 2004. 464 p.

[4] LERNER, M. I., SHAMANSKII, V. V., SAVELYEV, G. G. *Bulletin of Tomsk Polytechnic University*, 2007, V. 310,no 2. pp. 132-136.

[5] LERNER, M. I., SVAROVSKAYA, N. V., PSAKHE, S. G., BAKINA, O. V. *The technology of production, characteristics and some field of metal electric blasting nanopowders use (Russian nanotechnologies)*, 2009, V. 4.no. 9 pp. 6-18.

[6] LERNER, M., VOROZHTSOV, A., GUSEINOV Sh., STOROZHENKO, P. Chapter 4. Metal Nanopowders Production *(The book: "Metal Nanopowders: Production, Characterization and Energetic Applications")*, 2014, 440 p.

[7] IKONNIKOVA, K. V., IKONNIKOVA, L. F., KOLTUNOVA, E. A. *Procedia Chemistry*, 2015, vol. 15, pp 167-173.

[8] IKONNIKOVA, K. V., IKONNIKOVA, L. F., KOLTUNOVA, E. A. *Key Engineering Materials: Scientific Journal,* 2016, vol. 683, pp. 301-305.

[9] IKONNIKOVA, L. F., IKONNIKOVA, K. V., KOLTUNOVA, E. A. *MATEC Web of Conferences* (The 2nd International Youth Forum “Smart Grids”), 2014, vol.19. 01017 p. 3.

[10] NAUMOVA, E. N., KALINKOV, A. Yu., KOSTRZHITSKIY, A. I. Passivnye plenki na poverkhnosti konstruktsionnykh materialov i ikh zashchitnye svoistva. *Kholodil'na Tekhnika i Tekhnologiya*, 2001, no. 5 (74), pp. 46-51.

[11] GUBIN, S. P., KOKSHAROV, Yu. A., KHOMUTOV, G. B., YURKOV, G. Yu. Magnitnye nanochastitsy: metody polucheniya, stroenie i svoistva. *Uspekhi Khimi*, 2005, 74(6), pp. 539-574.

[12] KOSTRZHITSKII, A. I., CHEBAN, T. V., PODOLYAN, R. A. Oksidnye plenki na poverkhnosti zheleza i ikh fiziko-khimicheskie kharakteristiki. *Elektronnaya Obrabotka Materialov*, 2007, no. 3, pp. 50–55.

[13] LYUBUTIN, I. S., STARCHIKOV, S. S., DUBINSKAYA, Yu. L., LIN C.-R. Cintez, magnitnye i elektronnye svoistva nanokompozitov s zadannym sootnosheniem faz gematit-magnetit, effekty poverkhnosti. *V-ya Vserossiiskaya konferentsiya po nanomaterialam, NANO-2013, Zvenigorod*, 2013, pp. 314.

[14] TOLOCHKO, O. V., LI, D. V., KIM, B. K. Fazovye prevrashcheniya i magnitnye svoistva nanochastits na osnove zheleza pri termicheskoi obrabotke v okislitel'noi atmosphere. *Vestnik Novgorodskogo Gosudarstvennogo universiteta*, 2009, no. 50, pp.13-18.

[15] McBAIN, S. C., YIU, H. H., DOBSON, J. L. Magnetic nanoparticles for gene and drug delivery. *J. Nanomedicine*. 2008. vol 3(2). pp. 169-180.

[16] CORNELL, R. M., SCHWERTMANN, U. *The Iron Oxides: Structure, properties, reactions, occurences and uses. Second edition.* Weinheim, Willey-VCH Verlag GmbH & Co. KGaA. 2003. 683 p.

[17] ZHIGAL'SKIJ, A. A, IKONNIKOVA, L. F., MINAKOVA, T. S., MUKHACHEV, V. A., TROYAN, P. E. Temperature dependence of the dielectric strength of zinc sulfide films. *Russian Physics Journal*, 1996, *v*ol. 39. (6). pp. 576-578.

[18] SHEPOTKO, M. L., DAVYDOV, A. A. Priroda tsentrov poverkhnosti α-Fe_2O_3. *Zhurnal Prikladnoi Spektroskopii*. 1991, vol 54, no. 3. pp. 480-485.

[19] DAVYDOV, A. A. *IK- spektroskopiya v khimii poverkhnosti okislov.* N.: Nauka, 1984. 245 p.

[20] BAZHANOVA, A. G., KALAEVA, S. Z., MAKAROV, V. M. Opredelenie kharaktera funktsional'nykh grupp na poverkhnosti magnetita. *Zhurnal Khimiya i Khimicheskaya Tekhnologiya,* 2009. vol 52,no. 10, pp. 151-152.

[21] KUZNETSOVA, T. V., KUDRYASHOV, I. V., TIMASHEV, V. V. *Fizicheskaya khimiya vyazhushchikh materialov: Uchebnik dlya khim.-tekhnol. spets. vuzov.* M.: Vyssh.shk., 1989. 384 p.