THE OPTIMAL DOLOMITE PARTICLES SIZE ADDED TO THE ACRYLIC COATING OF BOOKBINDING CANVASES

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Abstract: *The aim of this research was to find the optimal size of the dolomite particles added to the acrylic coating for use on book canvas. To increase durability and resistance of archived books from acid environment, milled dolomite was used as an alkaline buffering agent. It was found that rough dolomite particles increase the surface roughness and worsen the mechanical properties of canvas, especially abrasion. However, they also most significantly alkalize and buffer the canvas surface in aqueous environment. The optimum size of the dolomite particles in the coating was achieved by balancing these properties.*

Keywords: *dolomite, canvas, coating, alkaline reserve, abrasion, roughness.*

1 INTRODUCTION

Books in archives and library collections are exposed to chemical [1], biological [2] and physical [3] effects. It leads to their damage during their archivation [4]. Due to these effects, we lose the valuable cultural heritage and knowledge recorded in the books. Repair of book bindings is very costly and labor intensive [5]. Additives in the coating may affect some properties of canvases, e.g., strength [6, 7], abrasion [8], resistance to insects and fungi [9], combustibility [10], etc. Due to environmental pollution, the air usually contains acid-generating oxides [1] (mainly sulphur dioxide) and a lot of inorganic and organic compounds. In the air of archives and libraries, volatile organic compounds such as benzene, toluene, ethylbenzene, xylenes or furfural which are a known marker of paper degradation are usually detected [11]. Alkaline reserve with buffering ability such as carbonates of alkaline earth metals (calcium carbonate, magnesium carbonate, calcium magnesium carbonate or dolomite) can also help to avoid a prolonged exposure to an acidic environment, which, in conjunction with moisture leads to acid hydrolysis. The consequence of acid hydrolysis of cellulose [12] is the loss of strength and decreased durability of paper and bookbinding canvas of archived books [13].

The fundamental challenge was to find the ideal size of the particles to be used as an additive to dual-layer acrylate coating. Too large particles of carbonate mineral worsen the look and touch feelings and increases surface abrasion of the canvas, which leads to its premature mechanical damage [14]. On the other hand, too small particles in the coating can be covered in large part by surrounding acrylate and may not exhibit sufficient activity in the surface contact of canvas with moisture and acid air. Since it is difficult to imitate the conditions in the archive, including effect of time [15], the simulation of negative factors of the environment was very simplified. We used milled and washed dolomite with different particle size (in range from hundreds of nanometers to tens of micrometers) as alkaline buffering additive [16] to the acrylate coating to create the bookbinding canvas with extended life. We examined the appearance and surface roughness of created canvases by image analysis. Subsequently, these samples were exposed to an aqueous environment where followed the changes in pH environment caused by the gradual release of dolomite over several days. Furthermore, we evaluated their buffering capacity in the gradual acidification by airy carbon dioxide. Finally, we concluded the optimal size of particles used in the coating regarding chemical and mechanical requirements of the developed book canvas.

2 EXPERIMENTAL PART

2.1 Material

Cotton fabric Sara (Licolor, CZ), area weight 135 g/m^2, fabric thickness 0.37 mm; Acronal S 996 S (BASF SE, GE) - aqueous polymer dispersion based on ester of acrylic acid and styrene, viscosity 2 Ns/m^2; granulated natural pink dolomite (anhydrous calcium magnesium carbonate, $CaMg(CO_3)_2$) for agricultural use (Forestina, CZ); TSA (Tryptic soy agar) in Petri dishes (BioVendor, CZ); Martindale abrasive cloth SM 25 (James Heal, England), ISO 12947-1:1998 [17].

2.2 Methods and devices

Commercial pink dolomite for agricultural use was dosed into cartridges of ball mill with zirconia balls of 1 cm diameter. Ten milling cycles (each of 5 min) with cooling intervals was carried out at 800 rpm. The dolomite was subsequently separated using different speeds of sedimentation of the particles in a glass cylinder filled with water to four fractions with different particle sizes. The resulting particle size of dolomite was measured using the particle size analyzer and laser scattering device (HORIBA LA-920, JP).

Each fraction was added to Acronal in an amount of 3% by weight of the coating paste, mixed thoroughly and these homogenized mixtures were used for coating of cotton fabric. Canvases were prepared using a laboratory coating device. All canvases were coated with two layers of coating and then condensed at 140°C for 2 minutes and dried at 100°C for 15 minutes.

The surfaces of coated canvases were scanned using the 3D digital multifunction microscope HIROX RH 2000 (MXB 2500REZ lens, diffuse adapter). Surface roughness (Rz) measurement was provided in accordance with Japanese Industry Standard (JIS) B0601 (1994) [18]. Rz is the sum of the average absolute value of the height (five highest peaks) and the average absolute value of the depth (five lowest valleys from the average line of the roughness curve) on the weft yarn, in micrometers. Ten-spot average roughness was chosen at zoom 1000x.

Fifteen cm^2 of each canvas including the reference sample (cotton fabric coated with acrylic coating without dolomite) was immersed in 50 ml of purified deionized water for several days at 22±2°C and its pH changes were continuously potentiometrically measured using glass silver chloride reference electrode.

Bacteriological control of water purity was carried out by a simple test, when 1 ml of water from each sample was inoculated on the agar (TSA) in Petri dishes. It was incubated for 24 hours at 37°C and subsequently bacterial colonies (CFU) were counted.

The abrasion resistance of canvas surface was tested according to the standard ISO 5470-2: 2003 [19] using Martindale Abrasion and pilling tester device (James H. Heal and Co. Ltd. England). Four circular samples with a diameter of 37 mm from each canvas were clamped in holders of Martindale device together with the pad of foam material, each with a down pressure of 12 kPa. Face (coated) side of canvases has been tested with the speed of about 60 rpm. The testing was performed using special Martindale abrasive cloth. In accordance with the standard [19] the abrading face side of canvases was controlled and visually evaluated according to a standardized scale (grade 0-5) in the following checkpoints: 1600, 3200, 6400, 12800, 25600 and 51200 abrasive revolutions.

2.3 Results

Result of particle size measurement using device HORIBA LA-920 (Figure 1) shows that after ten milling cycles in nano mill with zirconia balls the particle size of dolomite ranged from about 0.5 to 50 μm.

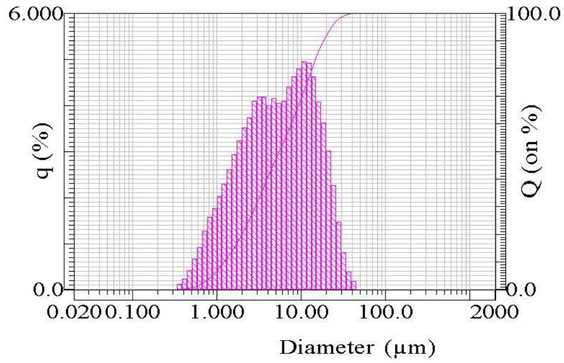

Figure 1 Distribution of dolomite particle sizes after 10 milling cycles in nano mill with zirconia balls

Figure 2 shows that particles of milled dolomite were sorted into 4 parts with the size of about 1 μm, a few micrometers and tens of micrometers based on the different sedimentation velocity of particles in the water column. These particles were used as an additive to the acrylic coating of cotton fabric, to give the four canvases with different roughness (Figure 3).

Table 1 Roughness of canvases No. 0-4 measured at magnification of 1000

	Canvas No.				
Rz JIS [μm]	**0**	**1**	**2**	**3**	**4**
Minimum	10.1	10.2	13.7	13.2	35.7
Maximum	10.8	17.5	21.5	27.8	39.0
Avarage	**10.44**	**14.48**	**17.12**	**24.2**	**37.14**
Median	10.4	16.9	14.8	26.9	36.6
S.d.	0.27	3.42	3.51	5.56	1.36

An overview of roughness coefficients (Table 1) confirmed the touch feeling of coating whose roughness increased with the addition of larger particles of dolomite.

Table 2 Abrasive properties of canvases No.0-4

Canvas No.	Grade of abrasion in the checkpoint					
	1600	*3200*	*6400*	*12800*	*25600*	*51200*
0	0	0	0	1	1	1
1	0	0	0	1	1	1
2	0	0	0	1	1	1
3	0	0	1	1-2	2	2
4	0	1	2	3	3-4	4

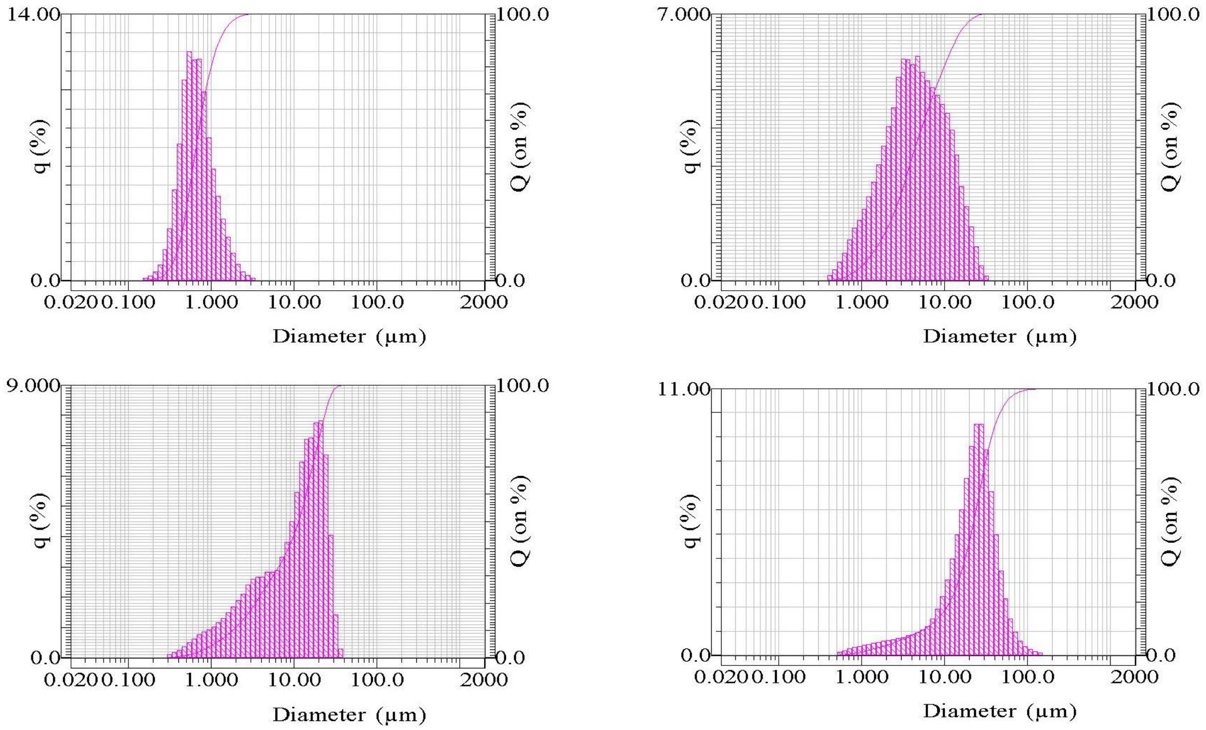

Figure 2 Four dolomite fractions sedimented in a glass cylinder with water during 1 to 24 hours. The average particle size: 0.75 (top left) – 6.20 (top right) – 12.30 (bottom left) – 48.60 μm (bottom right)

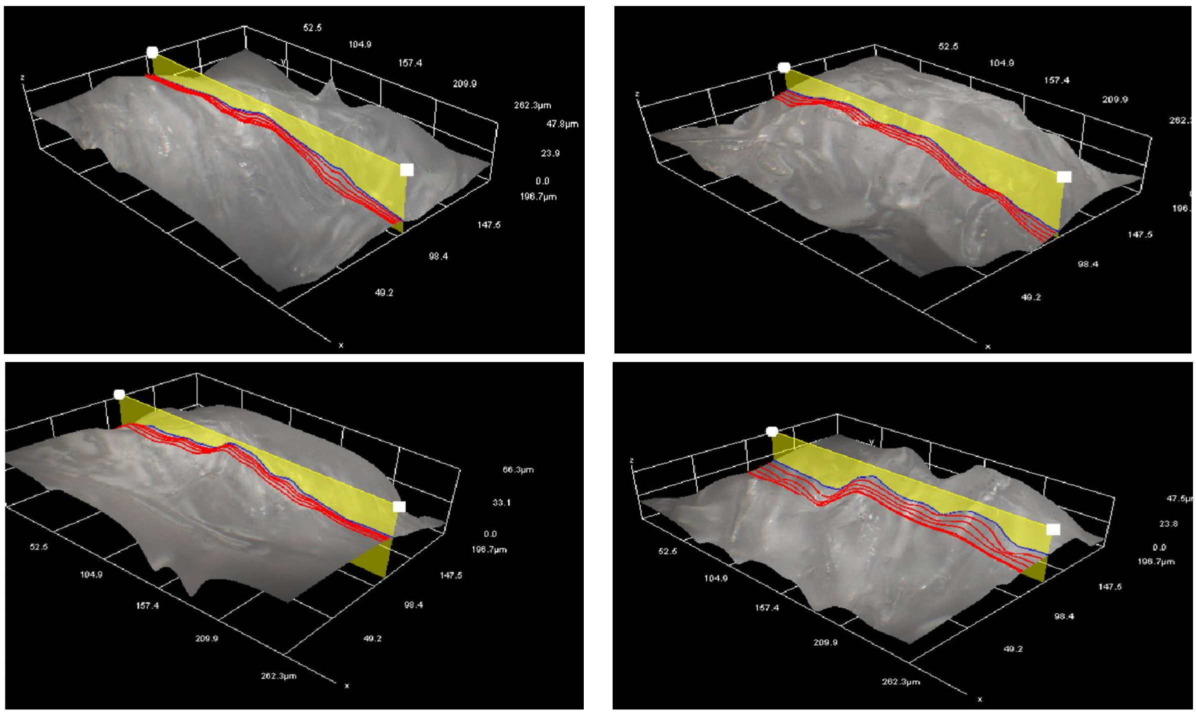

Figure 3 3D images of canvas surfaces: canvas No.1 (top left) – canvas No.2 (top right) – canvas No.3 (bottom left) – canvas No.4 (bottom right), zoom 1000x

Figure 4 shows the changes of pH in the water in which these canvases were inserted for 17 days. Fabrics with increasing particle size of dolomite in the coating were labeled No. 1-4. Canvas with acrylic coating without addition of dolomite is marked by zero, basic solution without canvas (purified water for injection) was marked by *A*.

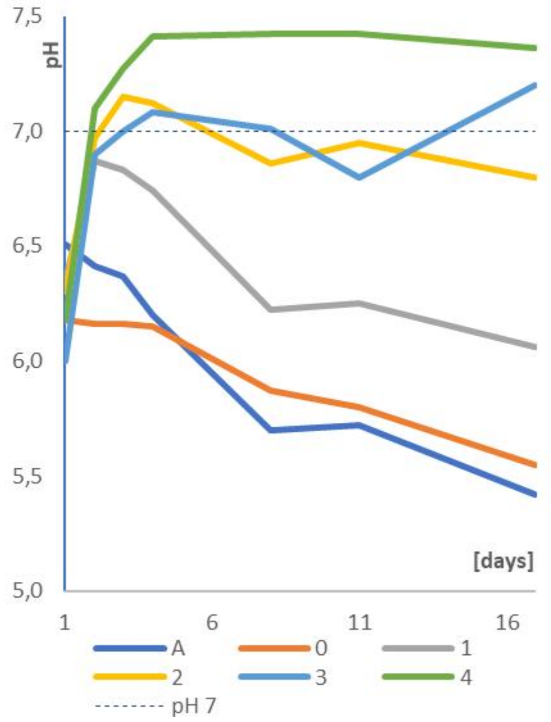

Figure 4 Changes of pH in aqueous solutions containing canvases with increasing particle size in the coating (1-4) for 17 days. Reference samples: 0 (canvas without dolomite in the coating), *A* (only water without canvas)

3 DISCUSSION

Different sedimentation rate of dolomite particles with different sizes and weight in the water column allowed their separation into four groups, with an average particle size of about 1, 6, 12 and 48 µm. Different roughness of canvases with coating containing these particles was distinguishable by the touch. Calculation based on 5 measurements of surfaces using 3D microscope differentiated these average roughness value from 10.44 to 37.14 µm. It is evident from Figure 4 that pH value in water samples containing canvases No. 1-4 increased in the early days. From about 4th day pH value in samples A, 0, 1 and 2 began decrease. Test of water bacteriological purity of all samples was conducted out the eighth and seventeenth day of the experiment. The suspicion that the pH value decreased due to bacteriological contamination was not confirmed (the number of grown bacteria was less than 5 CFU/1 ml). The cause of pH decrease in aqueous samples was therefore influence of atmospheric CO_2 (beakers with canvases immersed in water were not closed). Airy carbon dioxide dissolves slowly in water to form carbonic acid, which results in decrease of pH. As shown in Figure 4, pH of the sample 3 began to decrease slightly from the 8th day, the sample pH 4 from the 17th day. Samples No.3 and 4 (samples with the largest dolomite particles in the coating) alkalized and buffered the acidification caused by the influence of CO_2 for longer time and efficiently. This chemical process can be expressed by equations (1) and (2) [20]

$$CaCO_3 + CO_2 + H_2O = Ca(HCO_3)_2 \quad (1)$$

$$MgCO_3 + CO_2 + H_2O = Mg(HCO_3)_2 \quad (2)$$

As expected, abrasion tests on Martindale device showed that the canvas No. 4 with dolomite particle size of tens of micrometers in coating had the worst abrasion properties (Table 2). It achieved grade 4 (it means significant damage: the cover coating was broken and the middle layer was disturbed) at the last checkpoint. It is therefore unsuitable for use as a bookbinding canvas, because it would be very soon mechanically damaged and aesthetically unsightly (capture of dirt). Canvases No. 3, 2 and 1 however, exhibited good abrasion properties (grade 1-2, it means very slight to moderate damage with a change of gloss and no or only slight damage of the coating).

4 CONCLUSION

The aim of this research was to determine the optimum particle size of the powdered additive in the acrylic coating of canvas. The expected characteristics were alkalizing (buffering) ability in the moisture, and good mechanical properties, particularly an acceptable abrasion. We chose milled dolomite, whose particles had a size from several hundred of nanometers to several tens of micrometers. We added it into coating in concentration of 3 wt.% of the acrylic paste. We ascertained that the best properties of alkaline reserve met dolomite with particle size of tens of micrometers (canvas No. 4). However, this particle size also very worsened the canvas abrasion. Relatively good long-term buffering capacity was observed in canvas No. 2 with coating containing the dolomite fraction with particle diameter from 1 to 20 µm (average 6.2 µm, median 4.5 µm) and where 70% of particles ranged between 2 and 10 µm. This canvas maintained the pH of aqueous solution in the range from 6.9 to 7.15 for 17 days and met very good nonabrasive properties, because it reached grade 1 only (loss of gloss without damage) at the endpoint (51 200 rpm). We are convinced that the dolomite with particle size between 2 and 10 µm in 3% concentration is very suitable additive to the coating of bookbinding canvases with extended lifetime for archiving as well as borrowing mode.

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