

BEHAVIOUR OF METHYLCELLULOSE GEL AT HIGHER CONCENTRATIONS FOR CLEANING OF ACRYLIC PAINTED SURFACES

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Abstract. *This research demonstrates the application of methylcellulose (MC) as a gelator for cleaning acrylic painted surfaces. Highly thickened methylcellulose gels were predominantly tested to investigate the residue left after cleaning. The function of methylcellulose as a molecular trap was also assessed to minimize the clearance issue. The presence of residue, the efficacy of the methylcellulose as a cleaning agent and its physical impact on the paint surfaces were investigated using a digital microscope in normal, raking, and ultraviolet lights. Scanning electron microscopy (SEM), coupled with energy-dispersive X-ray spectroscopy (EDS) was used to study the compositional and topographical changes on the paint surface. Fourier transform infrared spectroscopy (FTIR) was performed in attenuated total reflectance (ATR) mode to observe the presence of residues after complete removal of the gelling agent. The experimental results indicated a minimum interaction of methylcellulose on the paint surface as the concentration increases in the gel formulation. The super-thickened hydrogels also worked like molecular traps useful for removal of soiling from the painted surfaces.*

Keywords: *methylcellulose; hydrogel; acrylic paint; cleaning; SEM-EDS; FTIR.*

1. INTRODUCTION

Methylcellulose (MC) is one of the most extensively used cellulose ethers in the field of conservation for various purposes such as adhesive for paper objects, consolidant for flaking media, for removal of old paper repairs, etc. It is also one of the most popular gelling agents used for aqueous cleaning formulations and is the simplest of all cellulose ethers. The amphiphilic properties (water soluble and organo-soluble) of methylcellulose are dependent on the degree of substitution (DS). The degree of substitution of MC varies between 0 and 3; when the DS is 0.1 to 1.1, MC is soluble in dilute sodium hydroxide and when the DS is 1.4 to 2.0 it is soluble in water and MC at this DS range of 1.4 to 2.0 is commercially available. In addition, when the DS is between 2.4 to 2.8, it becomes insoluble in water but is soluble in organic solvents [1]. MC behaves like a lower critical solution temperature polymer. It is soluble only in cold water; however, upon heating, the solution experiences a slight decrease in viscosity. On the other hand, when the MC solution is subjected to an increase in temperature over a prolonged period of time, the viscosity of the solution increases and a thermo-reversible gel is formed [2]. Generally, methylcellulose is synthesized by chemical etherification of cellulose with a methyl functional group available for substitution. The

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hydroxyl group are then responsible for the hydrophilic behaviour of MC that can be observed in aqueous systems [1].

Cellulose ethers are effective in modifying the surface properties of water. They can increase the solvents cleaning power and can also prevent various solvents from spreading across the surface during a localized cleaning. Cellulose ethers can also remove surface dirt by acting as a mild surfactant since they produce foam when used in low concentrations in water such as 1-2%, applied with a brush and removed with cotton swabs. However, application of gel with a brush for foam generation can cause unnecessary mechanical stress and also gives a hazy view of the cleaning action on the support [3]. The viscosity of methylcellulose as a function of temperature is dependent on its shear rates. The solutions of methylcellulose at low temperatures exhibit the Newtonian flow and upon increasing the temperature over a critical temperature of 30°C, increases the shear rate and the solution starts showing non-Newtonian behaviour. The molecular weight of methyl cellulose also influences the estimation of critical temperature to a small degree. It behaves as a viscoelastic fluid at 20°C and the formation of gel takes place at 50°C [2]. It is stable at room temperature but upon addition of salts and additives, its gelling temperature increases. Polar organic solvents which are miscible with water such as alcohols and glycols also increase the gelling temperature of methylcellulose.

The conservation field has faced challenging problems associated with the cleaning of acrylic emulsion painting for several years. The main problems associated with these types of paint are due to their low glass transition temperature (TG) and low minimum film forming temperature (MFT) [4]. At low TG the film always remains tacky; grime and unwanted particulates are therefore more susceptible to adhering to the surface and becoming imbibed in the upper paint which has always been a great concern amongst the conservators [5, 6]. The other problem with acrylic paints is their tendency to swell both in aqueous and organic solvents. The swelling of acrylic paint with solvents is dependent on their position in the polarity scale. It is minimum on both the higher and lower ends of the polarity scale with maximum swelling by chlorinated solvents and aromatics [7]. Since surfactants are added as an additive in the paint formulation and acrylic resins are dispersed in water, therefore both hydrophilic and hydrophobic portions are present in the bulk paint film and they interact with both water and organic solvents [8]. Hydrocarbon solvents, especially aliphatic hydrocarbons have been reported to cause less swelling for these types of paints; however, these solvents are not always efficient at removing the surface grime and other types of unwanted particulates [9]. Several studies have been conducted to understand cleaning efficiency and efficacy using vibrational spectroscopy, scanning electron microscopy (SEM), coupled with energy-dispersive X-ray spectroscopy (EDS), environmental scanning electron microscopy (ESEM), atomic force microscopy (AFM) etc. [6, 10-20] and have reported the swelling tendency as well as solvent sensitivity associated with a range of organic solvents. Gels may provide a solution that can control the movement of solvents and water on the paint surface, however, the potential for creating residues has always been an issue associated with physical gels and protocols used for clearance [21].

The main objective of this research is to evaluate the suitability of methylcellulose as a super-saturated gelling system for controlling the release of water, reducing the swelling of the paint films, serving as an effective cleaning system, and to minimize the presence of residues left behind. Changes in the appearance of the painted surface (*e.g.*, morphology, topography, etc.), as well as the relative ease of removal for various MC gel formulations, were assessed and recorded as well. Visual analysis, digital microscopy and ultraviolet fluorescence microscopy were employed to observe the cleaning effects on the surface before and after applications. A scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDS) was used to monitor the changes in elemental composition and for

imaging of the paint surfaces at higher magnifications. Fourier transform infrared spectroscopy in attenuated reflectance mode (ATR-FTIR) was used for assessing the presence of functional groups in methylcellulose residues and swelling of the paint surfaces after cleaning operation.

2. MATERIALS AND METHODS

2.1. PREPARATION OF PAINTED CANVAS SAMPLES

The painted canvas samples were prepared by using cadmium yellow paint from the Camel paint brand on the medium grained (textured), pre-primed, acid-free cotton duck canvas. The paint was applied on the canvas surface using a drag-down technique, specifically designed with local materials to achieve the even thickness throughout the paint film on all samples. The dry thickness of paint was measured with a micrometer and was found to be 100 ± 20 μm . All samples were kept for drying in museum condition for a period of six months. One canvas painting (2 x 3 ft) was also prepared in acrylic medium using various colours. The painted canvas was soiled artificially, simulating the museum dirt and its composition as mentioned elsewhere [11, 12].

2.2. PREPARATION OF METHYLCELLULOSE HYDROGELS

Methylcellulose of 4000 cps was selected for the analysis. It was decided that methylcellulose batches of different viscosities and concentrations would be prepared. MC of 5, 10, 15, 20 and 25% by weight was prepared. Deionized water was pre-heated to 100°C in a glass beaker on the induction cook-top ware. Methylcellulose powder of desired concentration was then mixed in hot water in w/v ratio. Its particles were immediately dispersed in the hot water to form a white turbid solution. The solution was stirred with a glass rod for half an hour and allowed to cool. All prepared batches of gels were covered and left for 48 hours for complete hydration, and then it was applied on prepared acrylic emulsion painted sample surfaces directly with a steel spatula. In total five concentrations of methylcellulose were used and gels of each concentration were used on five samples. Gels on all samples were allowed to stay for fifteen minutes to observe the maximum effect, if any, on the painted surface. After fifteen minutes the gels were removed from the painted samples using the wooden swab sticks. Further, the cleaned surface was dry cleaned with dry cotton swabs.

3.3. ANALYTICAL TECHNIQUES

FTIR qualitative investigation were performed using a Nicolet i550 spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) equipped with a Spectra-Tech ATR objective with diamond crystal. Ample pressure was exerted on the paint samples to flatten the canvas weave structure in order to compensate for the bubbles in the paint surface. All the samples were scanned with 4 cm^{-1} resolution averaged over 15 scans. FTIR spectrum was obtained in the wavenumber region between $4000\text{--}600\text{ cm}^{-1}$ and the resulting characteristic peaks were

recorded in absorbance mode. No corrections were made to any spectra. Data were compared with Essential FTIR v3.50.114 from Operant LLC software.

For the comparison of surfaces of samples before and after gel application, Dinolite 7915MZT Dino-Lite (Dino-Lite Europe/IDCP B.V., Almere, Netherlands) edge normal microscope was used and the images were taken at 5 megapixels in normal and raking light. Ultraviolet fluorescence microscopy was done by attaching a UV torch to the microscope. All the sample surfaces were micro-photographed at 50x magnification.

SEM images were captured using Carl Zeiss EVO 50 scanning electron microscope (Carl Zeiss AG, Jena, Germany) at 100x, 250x, 500x and 1000x magnification at high vacuum mode. For SEM imaging, samples were gold coated. For EDX analysis, the samples were carbon sputtered and the data processed with Roentag software. The accelerating voltage was set at 20 kV at a working distance of 8 mm at a resolution of 2250 nm.

3. RESULTS AND DISCUSSION

On visual observation, it was noticed that methylcellulose at higher percentages was very effective in controlling the release of water thereby sufficient moistening the painted surface for the soil to stick to the gel. Only dry cotton swabs were used to remove the gels and no other clearance step was done for removal of the gels. Pigment loss was noticed in cotton swabs in all samples cleaned with MC 5% gel. Loss of pigment was also noticed in all samples cleaned with MC 10%, though in two samples the loss was very less. Samples cleaned with MC15% also showed minor pigment loss in the cotton swabs. However, in the samples cleaned with MC 20% and MC 25%, there was no pigment loss noticed in the cotton swabs. The removal of gels from the samples cleaned with MC 5% and MC 10% were very easy, swabbing was continued till the time all gels were lifted completely to the unaided eye since the gels at these concentrations were less viscous and could not be removed in one step. MC 15% gel could be lifted from the samples with little pressure while removal of MC 20% and MC 25% required a considerable amount of force to pull the gel from the sample surfaces. It was noticed that MC at 15 and 20% concentrations held the sample surface very firmly and canvas got pulled along the gel during gel removing action (Fig. 1).



Figure 1. Canvas got pulled along the gel residue due to high adhesion at 15 and 20% concentration of MC gels.

It was also observed that the removal of the gel was better using cotton swab stick than with steel spatula. No water release was noticed with any concentration on the sample surface. Since the gels were allowed to stay for fifteen minutes on the sample surfaces, the swelling was noticed in many samples on visual observation (Fig. 2).

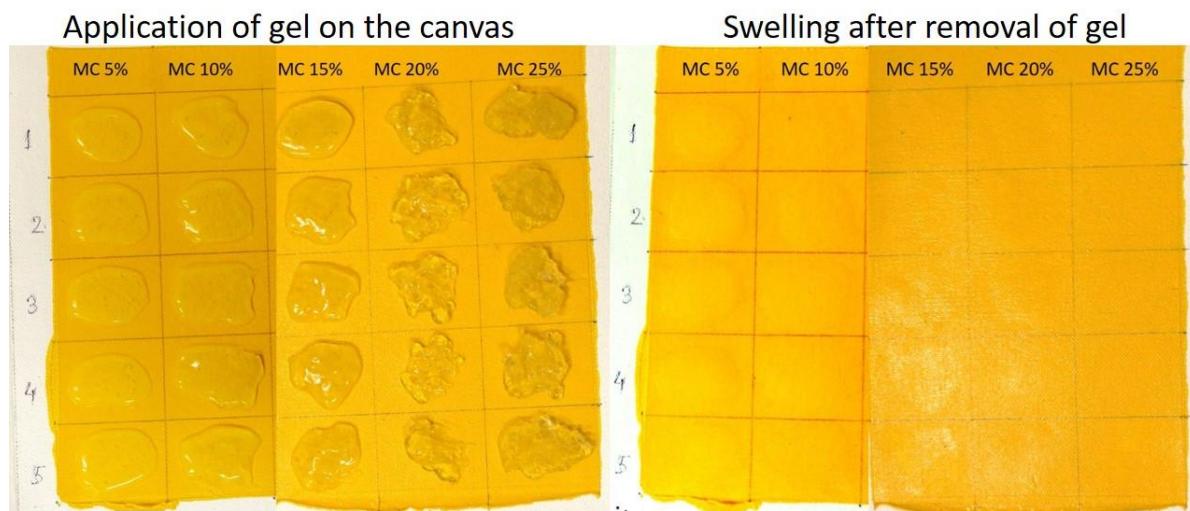


Figure 2. Application of gels at various concentrations on the painted canvas sample and swelling noticed in the canvas after the removal of the gels.

The swelling was very prominent in all samples cleaned with MC 5%. High degree of swelling was also noticed in all samples cleaned with MC 10%, though slightly less in comparison to the samples cleaned with MC 5%. The swelling was also observed in the samples cleaned with MC 15% and 20% to a lesser degree. However, no swelling was observed in any sample cleaned with MC 25%. This indicated that MC at 25% concentration, the rate of water release from the gel matrix was very slow and actually had very less amount of water in it. When the soiled sample surface was cleaned with all five concentrations, all showed similar cleaning efficacy on visual analysis. MC 20% and MC 25% gels were highly viscous and pulled the soiling into their gels. MC at 25% gel worked more like a molecular trap (Fig. 3).



Figure 3. MC at 25% concentration behaving as a molecular trap and lifting the dirt in its matrix.

This property of MC at 25% can be further explored for cleaning of the sensitive surface where minimal wetting is required to dislodge the dust and dirt as MC at this concentration can maintain very low levels of water and organic solvents in its gel network and also it is softer than the dry erasers as it contains water. However, the swelling was not observed after 24 hours and there was no apparent distortion in the surface of any of the samples. The images were compared in both normal light and ultraviolet radiations at 50x. Ultraviolet fluorescent photography revealed lots of cotton fibres stuck on two sample surfaces cleaned with MC 25% which probably reflected the edges of the cleaned area. Both UV and raking light images of the samples showed some cotton adhered on the sample surfaces (Fig. 4).



Figure 4. a) Image showing the presence of methylcellulose residue; b) image showing some pitting occurred with a digital microscope in sample cleaned with MC 10%; c) ultraviolet image showing some cotton fibres adhered on the sample cleaned with MC 25%.

4.1. ANALYSIS OF SURFACE COMPOSITION AND TOPOGRAPHY

The SEM images did not show any swelling or shrinkage induced cracks in any of the sample cleaned with any concentration of methylcellulose. The presence of migration of surfactants was not noticeable on any of the sample surfaces including the control samples. This indicated the less surfactant used in the paint composition. The paint surface also did not show any roughness which is usually noticed after solvent cleaning (Figure 5).

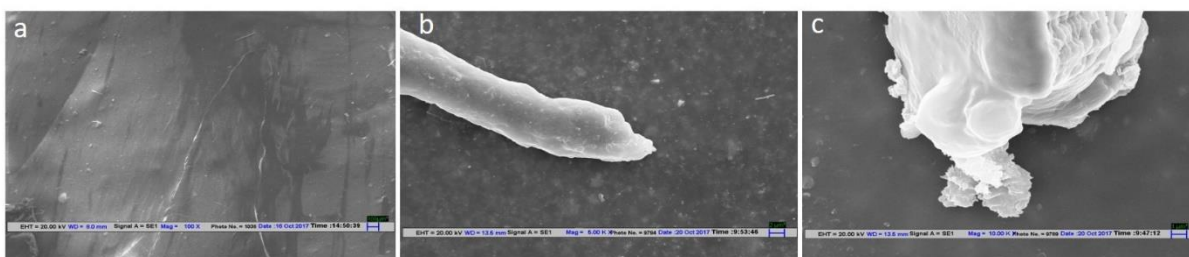


Figure 5. a) SEM image showing the gel residue in sample cleaned with MC 15% taken at 100x magnification; b) and c) SEM image showing the presence of methylcellulose residue in samples cleaned with MC 10% taken at 5000x magnification and 5% taken at 10000x magnification respectively.

This further indicated the gel cleaning method as a safer option to the other modes of cleaning. The distribution of elemental composition after cleaning was obtained with EDX analysis of all samples at 100x and 500x. In the EDX spectra of all samples, oxygen, carbon, cadmium and sulphur were detected as major elements and also the sodium, zinc and aluminium were detected as minor elements. The presence of cadmium and sulphur originated from the pigment used. The pattern of reduction of weight percentages of cadmium and sulphur in all cleaned samples when compared with control samples indicated the

pigment used is cadmium sulphide. The presence of sodium, zinc and aluminium may have also emanated from the extender used in the paint formulation. The presence of oxygen and carbon reflected the elements of the acrylic binder. When the distribution of cadmium and sulphur was compared at 100x, the weight percentages of cadmium and sulphur in the control sample were 21.21% and 6.73%, respectively, in the cleaned samples, the weight percentages of cadmium and sulphur was reduced to 6.35 and 1.37, respectively when cleaned with MC 5%, 7.51 and 3.47, respectively when cleaned with MC 10% and 7.12 and 2.0, respectively when cleaned with 15%. In the samples cleaned with MC 20%, the weight percentages of cadmium and sulphur were 11.52 and 3.26% respectively, which were slightly higher from the cleaned samples with MC 5, 10 and 15%. However, at MC 25 %, the weight percentage of these two elements was 19.39 and 6.04% which were almost similar to the weight percentages of the control sample. The reduction of weight percentages of cadmium and sulphur indicated the presence of residue in samples cleaned with MC 5, 10 and 15 %, also in MC 20%, though in a lesser amount and no presence of any residue in case of MC 25% which also supported the observed results during cleaning. EDX spectra obtained at 500x of all samples also showed similar trends in weight percentages. No EDX spectra showed any other elements present on the surface of cleaned samples which probably indicated little to no migration of any component from the bulk paint film (Table 1).

Table 1. Comparative evaluation of weight percentages of elemental compositions of control and samples cleaned with all concentrations of methylcellulose at 100x.

Element	Atomic Number	Series	Norm. C [Wt. %]					
			Control	MC 5%	MC 10%	MC 15%	MC 20%	MC 25%
Oxygen	8	K-series	36.61	51.87	50.12	49.05	48.32	39.05
Carbon	6	K-series	32.11	38.41	37.96	39.68	35.62	32.69
Cadmium	48	L-series	21.21	6.35	7.51	7.12	11.52	19.39
Sulphur	16	K-series	6.73	1.37	3.47	2	3.26	6.04
Sodium	11	K-series	1.09	0	0.63	0	0.89	0
Aluminium	13	K-series	0.24	1.99	0.32	0	0.38	0
Zinc	30	K-series	2.01	0	0	2.15	0	2.83

4.2. ANALYSIS OF RESIDUES ON THE PAINT SURFACE AND PAINT SWELLING

The FTIR spectra of control sample and samples cleaned with methylcellulose in five concentrations viz. 5%, 10%, 15%, 20% and 25% were compared to evaluate the presence of residues left on the painted surface after cleaning. The FTIR spectra of control sample showed an intense strong peak of C-O-C stretching vibration at 1148 cm^{-1} , the two less intense but well-defined peaks of C-H bending at 1382 cm^{-1} and 753 cm^{-1} attribute to the absorption vibrations of the methyl group. The band at 989 cm^{-1} , 1062 cm^{-1} and 844 cm^{-1} showed the characteristic absorption vibration of polymethyl methacrylate [22]. The C-H stretching frequencies were observed strong at 2955 cm^{-1} and a well-defined peak at 2874 cm^{-1} with a distinct shoulder at 2936 cm^{-1} . The presence of an intense and sharp peak of C=O stretching at 1725 cm^{-1} is attributed to acrylate carboxyl group [22]. All these frequencies of the C-H stretching bands at 2955 , 2874 cm^{-1} with a shoulder at 2936 cm^{-1} along with carbonyl bond stretching at 1725 cm^{-1} indicated the presence of an acrylic binder of poly *n*-butyl acrylate and polymethyl methacrylate co-polymer [23].

The FTIR spectra of samples cleaned with 5% and 10% showed a change in intensities and peak positions. Figure 6a showed a comparative study of samples cleaned with 5% and

10%. The peak position at 1148 cm^{-1} shifted to 1117 cm^{-1} which is one the characteristic bands of cellulose and related to C-C bonds of monomers of polysaccharide [24]. The intensity of the peak at 1065 cm^{-1} has shifted upwards which corresponds to C-O stretching vibration of methylcellulose. In both treated samples, along with the presence of the residue of methyl cellulose, the presence of cotton fibres loosely stuck on the paint layer also increases the intensity of the peaks. However, the samples cleaned at 5% and 10% showed a good resonance of related peaks probably due to the absorption vibrations of cotton fibres stuck with methylcellulose in samples of both concentrations. In the spectra obtained for samples cleaned with MC 15%, there is a shift in the peak positions from 2955 to 2905 cm^{-1} and 2838 cm^{-1} due to C-H stretching vibration which can be ascribed to the presence of CH and CH_2 of the cellulose and methyl group of methylcellulose [25] (Fig. 6).

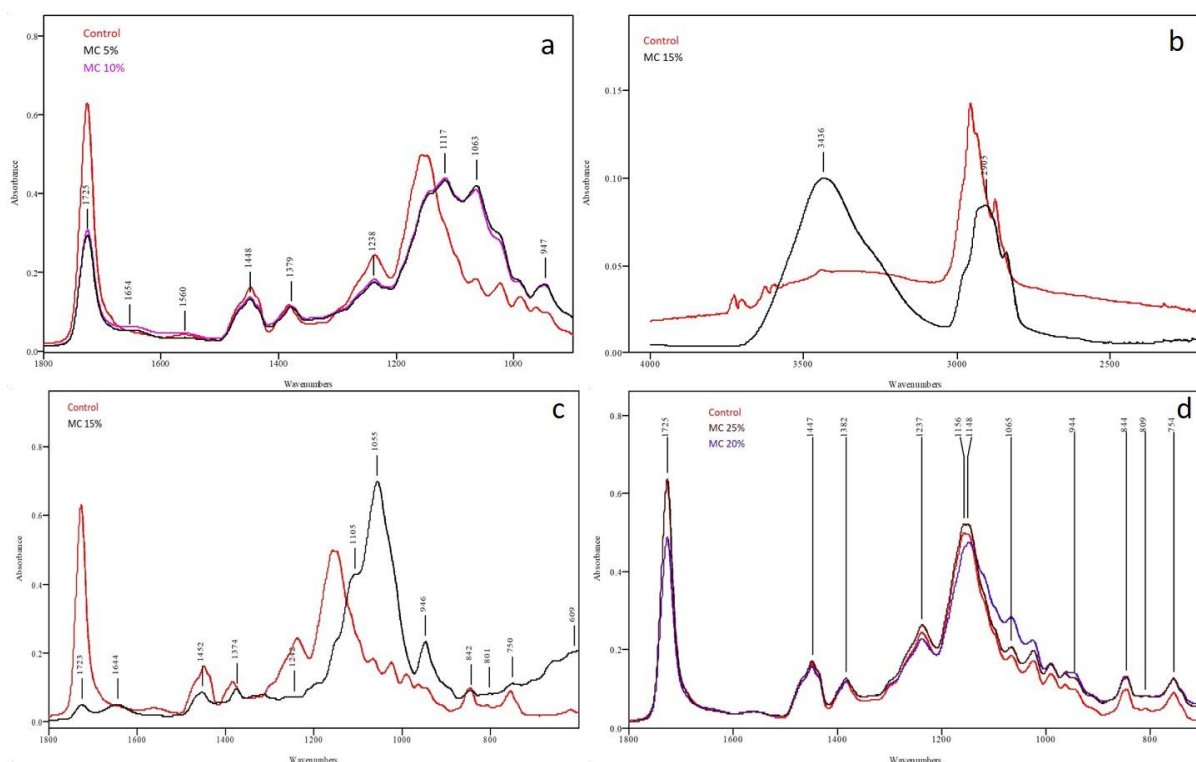


Figure 6. a) Comparative spectra in the fingerprint region of sample cleaned with MC 5% and MC 10% compared with control; b) Comparative spectra of control and sample cleaned with MC 15% showing the shift in peak positions; c) Comparative spectra in the fingerprint region of control and sample cleaned with MC 15%; d) Comparative spectra of the fingerprint region of control and sample cleaned with 20 and 25%.

The peaks present at 1452 cm^{-1} , 1374 cm^{-1} , 1314 cm^{-1} are due to C-H stretching of CH_2 and CH_3 groups. A faint peak of the C-O carbonyl stretching observed at 1644 cm^{-1} and a peak of OCH_3 ring stretching observed at 946 cm^{-1} . There is a peak at 1374 cm^{-1} of C-H bending which represents the methyl group. This peak also corresponds to methylcellulose [26-29]. The presence of a band at 1105 cm^{-1} indicates the presence of C-O-C stretching, characteristics of cellulose ethers. Again there is an intense peak at 1055 cm^{-1} which is due to C-O stretching vibration from the glucosidic units, a characteristic of methylcellulose (Figure 6c). There is also a broad peak at 3436 cm^{-1} which is due to O-H stretching vibration. This all indicated the presence of methylcellulose on the paint surface. The peak at 1725 cm^{-1} has been shifted to 1723 cm^{-1} and is highly suppressed, probably the residue of methyl group masked the peak. The spectra of samples cleaned with 20% and 25% showed similar results and all the peak positions of both samples were same when compared with the spectra of the control

sample (Fig. 6d). However, the spectrum of sample cleaned with 25% was very close to the spectra of the control sample (Fig. 7).

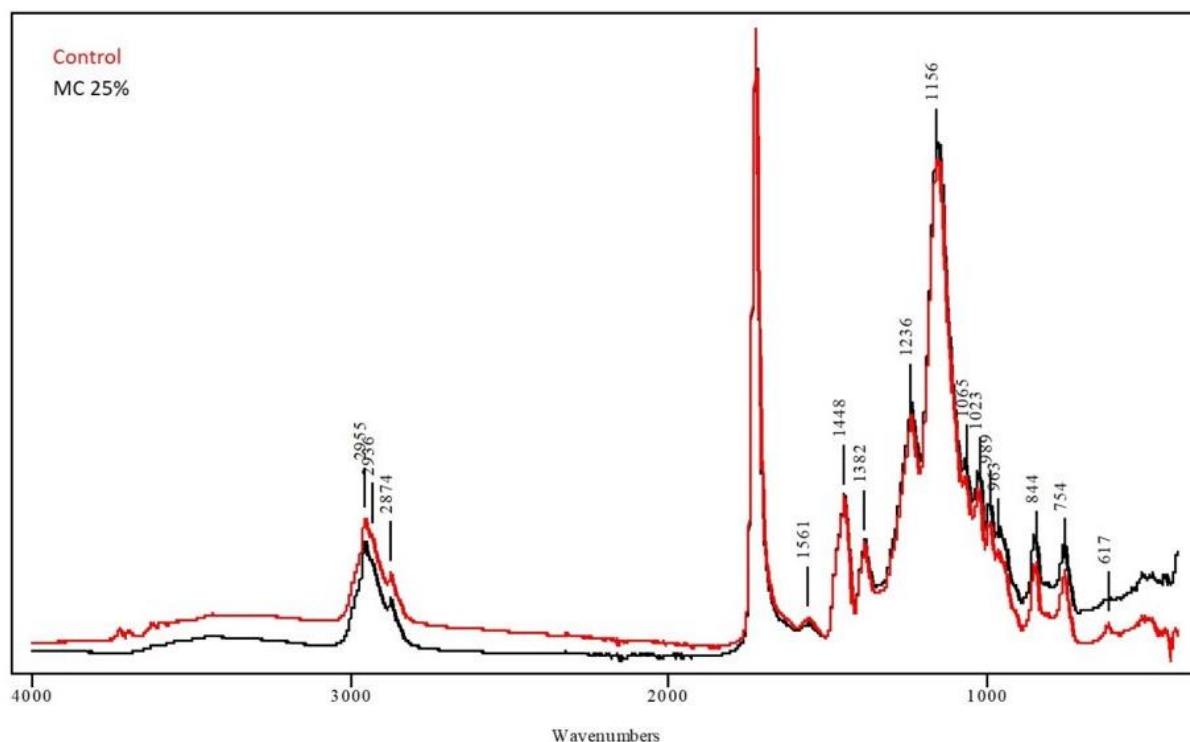


Figure 7. Comparative spectra of the fingerprint region of control and sample cleaned with MC 25%.

On comparing the intensities of the peaks at 1065 cm^{-1} which is due to C-O stretching vibration, it is evident that the sample cleaned with 25% was very identical to the profile of control. In case of sample cleaned with 20%, there was slightly upward shift, in all other three samples there is a drastic upward shift in the peak intensities which clearly showed the evidence of methylation (Fig. 8a). A good comparison for swelling of samples cleaned by MC of all concentrations was observed at 3436 cm^{-1} . The intensity of the peak of MC 25% was slightly lower to the control which probably indicated that the surface has become slightly drier. The peak of MC 20% was slightly upwards whereas, in the case of MC 5, 10 and 15%, their peaks showed highest absorption and broadening of the bands in this region. This clearly indicated the maximum swelling with MC 5, 10 and 15% (Fig. 8b).

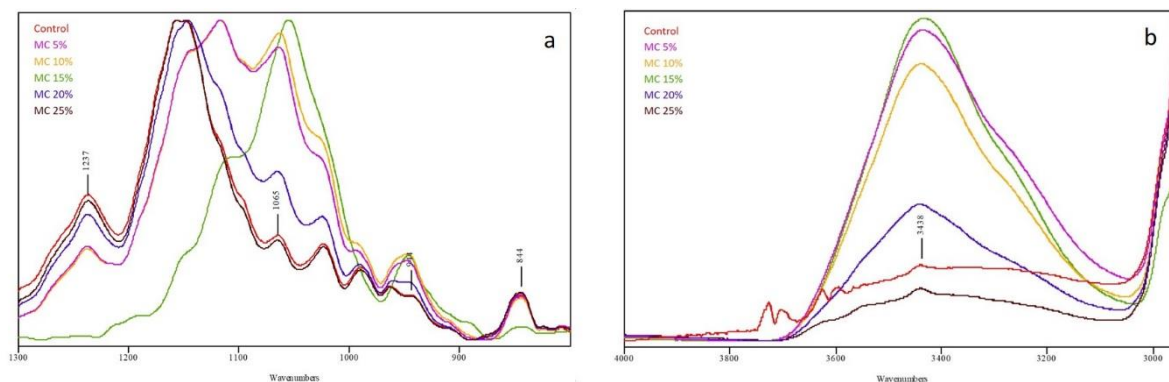


Figure 8. a) Comparative spectra of control and sample at the peak position 1065 cm^{-1} showing the evidence of methyl group; b) Comparative swelling of the paint films shown by the difference in intensity of the band at 3438 cm^{-1} .

5. CONCLUSIONS

Experimental results showed fewer amounts of residues of methylcellulose present on the sample surfaces when used in very high concentrations. MC at 25 % didn't leave any residue and entire gel from the surface was removed in one step. FTIR-ATR analysis indicated the presence of residues in samples cleaned with 5, 10 and 15%. It also indicated the presence of a minor amount of residue in the samples cleaned with MC 20%. However, FTIR spectra of samples cleaned with 25% showed none to minimal presence of residue. The swelling tendency was also reported by FTIR which showed no swelling in samples cleaned with 25 %, highest swelling with MC 5 % and 10 %.

SEM-EDS results showed depletion of cadmium levels in the samples cleaned with MC 5, 10, 15 and 20% pointing towards the presence of gel residues on these samples, whereas no such reduction in samples cleaned with MC 25 %. SEM images showed the gel residue on the paint film in all samples cleaned with MC 5 to 20 %. No residue was noticed in the samples cleaned with MC 25%.

Ultraviolet fluorescence microscopy in ultraviolet fluorescent mode, however, revealed some loose cotton fibres adhered which probably resulted due to development of some static charges. The usage of methylcellulose at very high concentrations and their function as wet molecular traps requires further exploration. This molecular trap can be used as a wet erasers which can function as an eraser but cannot burnish the paint surface due to presence of water in its matrix.

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