

DOI: 10.5281/zenodo.192843

# LOW COST PULPS WITH MICROEMULSIONS FOR CLEANING OF FRESCO PAINTING SURFACES

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Received: 03/10/2016

Accepted: 12/12/2016

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## ABSTRACT

Cleaning mural paintings using microemulsions were applied by means of export poultice technique (50:50) mixture of Arbocel BC 1000 and Arbocel BC 200 (type of pure cellulosic fibers). The cleaning fluid is added to pure cellulose until the saturation of pulp is converted into compress which apply to the cleaned surface. In current study, three global successful microemulsions were chosen to be used in cleaning models of fresco paintings from the monastery of saint Jeremiah using three kinds of available local low cost pulps (paper pulps – cotton fiber – wood mulch (sawdust)) instead of the Arbocel. The results are supported by optical microscope, and Fourier transform infrared (FTIR) spectra for the poultices after treatment to define the solubilizing spots in the compresses after treatment. The paper pulp is the most successful compress as it contained the wax and glue spots with the three kinds of microemulsions compared to sawdust and cotton fiber.

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**Keywords:** Fresco painting, Microemulsion, Cleaning, Paper pulp, Sawdust, Cotton fiber

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## 1. INTRODUCTION

Using microemulsion in cleaning surfaces proved their success since 1990. Microemulsion was developed by the CSGI (Centre for Colloid and Surface Science) in Italy, where Baglioni used the micro emulsions in cleaning in Brancacci's paintings. (Baglioni et al., 2012). He used also, microemulsion contained Triton 100 for first time for conservation of the mural painting in Vendel Church in Sweden (Garreau, 2007). On the other hand, Carritti et al., used microemulsion contained SDS in cleaning wall painting Loggia del Bigallo, Florence. (Carretti et al., 2005). In addition, Giorgio et al., used three kinds of microemulsions to remove Polaroid, primal and Mowlith resin (Giorgi et al., 2009). Carretti et al., studied the EAPC microemulsion in cleaning wall paintings in Mayapan. According to the traditional instructions in cleaning they used Dodecan in cleaning Salvador Church in Italy as there was a wax spots but they caused more distortion as the wax solubilized in Dodecan and penetrated in the mural painting surface after solvent evaporation, the wax was re-deposited within the pores (Carretti et al., 2005). In addition, to all abovementioned organic solvents are highly toxic, so they are considered as an environmental pollutants. Moreover, the organic solvents has an affect the skin, eyes and lungs of the user. After long time, it was conclude that the using organic solvents has disadvantages, due to it can attack the paint layer finally led to cause vital separation. (Domingues et al., 2013)

The advantage of microemulsion, it can remove hydrophobic layers using a small amount of organic solvent. Moreover, the microemulsion droplets contain the appropriate solvent able to swell or solubilize the polymeric layers, while the water in the dispersing phase can penetrate within the porous substrate of the artifacts, avoiding the risk of re-deposition of the dissolved polymers. Nanostructured fluids are using organic solvents to remove the undesired layers but in a very control way in micro emulsion or micelles or gel to avoid the disadvantage of pure organic solvents.

### 1.1 The current fresco painting

This fresco painting has a registration number (7968), at the National Museum of Egyptian Civilization (NMEC) in Fostat city, Cairo, Egypt. Its dimensions about 110 cm x 119 cm, the thickness about 4cm. It dates back to the 4th century and was discovered in 1907 by Qubille in Saqqara (Quibell, J.E., 1913).

## 1.2 THE UNDESIRED LAYER ON THE SURFACE

The undesired layer on the surface are due to the presence of glue on all pigments. The presence glue is attributed to the adding layers of glue for consolidation in the previous treatments and the wax spots.

## 2. MATERIALS AND METHODS

### 2.1 Materials

For the experimental work the following sodium dodecyl sulphate (SDS), pentanol-1 (PeOH), purified water, p-xylene and toluene were purchased from Sigma-Aldrich and were used as received. The order of mixing and the amount of materials are very important thing must be considered during the preparation methods (Baglioni et al., 2007).

### 2.2 Preparation of microemulsions

The O/W Microemulsion1 was prepared according to Baglioni This microemulsion is very important in cleaning fresco paintings by dispersing a given amount of Triton 100 (as indicated in Table 1) in an aqueous solution containing 46 ml of water stirred using the magnetic stirrer with 535 -540 RPM (round per minute) for one hour. The preparation were prepared according to published report. In brief, ammonium Carbonate was gradually added while stirring at 25°C. The system which is initially opalescent suddenly becomes limpid after a few minutes. Next the dispersed phase p-xylene was added the stirring process is continuous until the solution is totally transparent (Baglioni et al., 2012). For microemulsion 2 according to Carritti (Carretti et al., 2015) the SDS was added first to the water left on stirrer with 535-540 rpm for one hour. After solubilizing SDS the solution became milky, the 2 mg of 1-pantanol and 1 ml of p-xylene were added to the solution which turned to opaque. The stirring process takes place until the solution became completely transparent. For preparation of microemulsion 3, It was prepared according to Henri et al., who presented the composition of micro-emulsion 3 (Heneri, L. 1988). Microemulsion 3 was prepared via solubilizing 2g of SDS in 50 ml toluene through the stirring of solution at temperature 80°C for one hour with 600-700 rpm. After the solution became transparent a 2 mg of 1-pantanol and 1ml of water were added, the stirring process takes place until the solution became completely transparent.

Table 1 Composition (% w/w) of the Used Systems in removal of undesired layers:

ME 1		ME 2		ME 3	
Component	Composition	Component	Composition	Component	Composition
Purified water	46.3 ml	Purified water Surf. SDS	21.35 ml	Toluene	50 ml
Surf. Triton100	2.45 ml	p-Xylen	1.025gm	Surfactant SDS	2 mg
P-xylene	0.20 ml	1-Pentanol	0.65 ml	Purified water	2 ml
Ammonium carbonate	1.05 mg		1.975 mg	1-Pentanol	2 mg

### 2.3 Preparation of the mixed microemulsions with three local pulps

The three microemulsions were applied on three models using three available local kind of pulps (paper pulp, cotton fiber and sawdust) To apply the microemulsions in cleaning fresco paintings globally according to Carreti (Carretti et al., 2015). And the cleaning fluid is added to a powder made up of fibers or pure cellulose (50:50 mixture of Arbocel BC1000 and BC200 (kind of cellulose fiber) until saturation the pulp is converted in to compresses which apply to the cleaned surface. typical application time about 2.5 hours at temperature between  $29 \pm 0.5$  °C or at the room temperature were applied. The Japanese paper is located between the compress and the model surface to avoid direct contact between the cellulose fibers and the colored surface in order to eliminate the evaporation of the organic phase. The compresses are covered with commercial Polyethylene sheet. Once the compresses are removed the cleaned surface is washed by water to complete remove all residues of surfactant.

After presented the global method in application of microemulsion another local pulp can be used in application of microemulsion by using paper pulp preparing as following;

Bring papers free from acidity, cut them into a very small parts, soaked them in distilled water for 24 hour, squeeze the prepared pulp and totally dry it. The microemulsion is added to the prepared dried paper pulp. For using cotton fibers and the local sawdust by filled them with microemulsion.

There are many factors affect the success of microemulsion to remove the undesired layer such as:

- The kind of compress.
- The time of contact (the application time was two hours).
- The temperature was  $29.5 \text{ }^\circ\text{C} + 0.5$ .

After adding the three microemulsion to the three different pulps. The filled pulp was added to the three models of Coptic fresco paintings after putting Japanese paper on the paintings surfaces. Covering the pulps with commercial polyethylene sheet to eliminate the evaporation process of the microemulsion. Then left it on the surface for 2.5-3 hours at the room temperature. The most advantage of microemulsions is the dispersing amount of organic sol-

vents is less than the pure organic material and the effect of the organic materials on the uses is reduced in microemulsion 1, 2. But the microemulsion 3 is essentially to consist of organic material, so it must be used in case of the important and the with difficult spots only. After the defined time, the three layers (Japanese paper, pulp - polyethylene sheet) were removed. There is a good way in the cleaning with microemulsions by the direct use with cotton (as shown in Fig. 1C). But, the direct use of microemulsion must be under control to avoid any removing of painted layers.



Figure 1 (A) removal of the poultices during the cleaning procedures, (B) solubilization of undesired layer and immigration of undesired layer into the poultices and (C) removal of paint layer with the direct use of microemulsions.

### 3. RESULTS AND DISCUSSION

Figure 1 shows the using three local compress (in order to replace the Arbocel compress with available local compress), the application time was two hours and the temperature was  $29.5 \pm 0.5$  °C. After the defined time the Japanese paper with the commercial polyethylene and the filled pulp were removed and then the surface was cleaned several times with deionized water. This operation was carried out with the aid of cotton and brush. In Figure 2 displays that the ME 1 is the most effective in removing the undesired layers on the models and it is interesting to note that in similar tests the ME 2 didn't produce such good results. In case of ME 3, it was so effective in removing the undesired layer than ME 2 but according to the composition of W/O microemulsion. Due to the percent of organic material is high, so we prefer to use the O/W microemulsion in cleaning

fresco painting, but we can also use the W/O microemulsion in the necessary and difficult cases. The paper pulp and cotton fiber are more effective than the sawdust and the direct use of microemulsion is so effective as the undesired layers removed in only five minutes but must be used carefully and under control. But in cases the paint layer is so fragile or turned into a powder it can't be used.



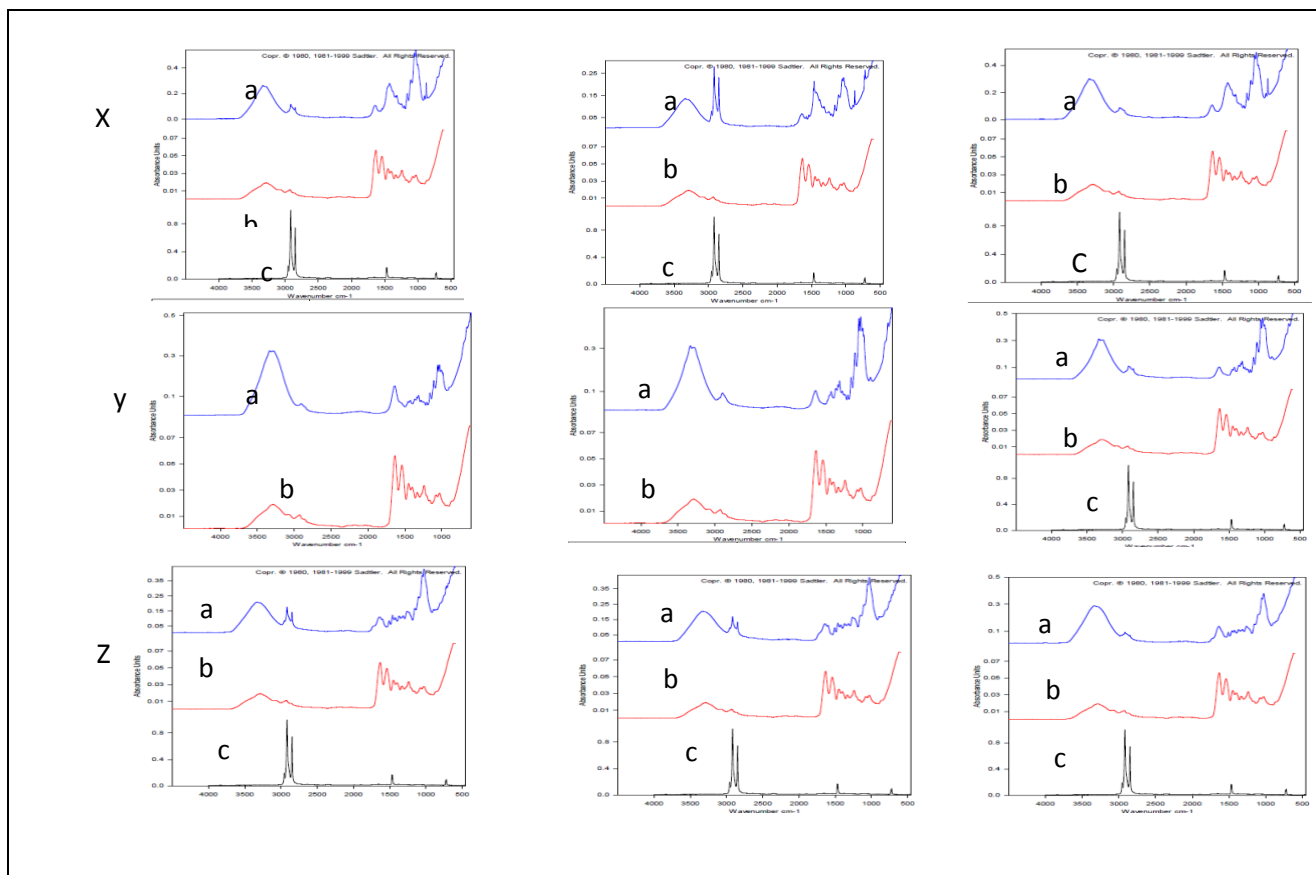
Figure 2 A, B and C, three models after cleaning with three kind of microemulsion filled in three kind of pulps.

### 3.1 Optical microscope

The purpose of using portable optical microscope is to identify the success of removing undesired layers away of the surfaces. **Table 2** shows the difference between the three microemulsions with three kinds of pulps. The First column illustrates the undesired layers on the surface of the models. The Second column express the results of the direct uses of the microemulsions which revealed that the direct use is very active as the undesired layer can be removed in only five minutes but must be applied carefully. The Third column illustrates the results of using the paper pulp filled with microemulsion. The Fourth column express the results of using cotton fiber, and the Fifth column illustrates the results of using sawdust. The direct use of the three microemulsions is very active and speedy but the direct use must be under a very good control to avoid any effect on the painted layer so the only case for using the direct use of microemulsions when the painted layer is very good. There aren't a very big difference between the paper pulp, cotton fiber and the sawdust , they are the same but the paper pulp and the cotton fiber are the easiest way for the application of microemulsion and more coherent even after the compresses were dried.

Table 2 Digital optical microscope images observed the result of using microemulsion.

The kind of ME	Before using ME	After the direct use	After the paper pulp use	After the cotton fiber use	After the sawdust
ME 1					
ME 2					
ME 3					
<b>Explanation</b>	The undesierd layers on the three models	The direct use of microemulsion using stick with cotton proved it's success in removing the undesierd layer in the three samples	The paper pulp with the microemulsion proved it's success in removing the undesierd layer in the three samples	The cotton fiber with the microemulsion proved it's success in removing the undesierd layer in only one sample	The sawdustwith the microemulsion proved it's success in removing the undesierd layer in the three samples



**Figure 3** X-Z FTIR spectra of paper pulp (x) with three kinds of microemulsion (y) Cotton fiber with three kinds of microemulsion (z) saw dust with three kinds of microemulsion. a) pulps with different ME, b) Animal glue and c) the paraffin wax.

### 3.2 Fourier transform infrared (FTIR)

The Three different pulps with three kinds of microemulsions were subjected to FTIR analysis in nine samples as shown in Fig. 3. The spectra shows a characterized peaks of the wax and glue, as confirmed by comparison with the spectra of a standard commercial glue and wax. (Fig. 3x) revealed that the three microemulsion with paper pulp could to solubilize the animal glue as a strong absorption of C-H stretching bands at 2850, 2919 and 3028 cm<sup>-1</sup>, C-O stretch at 1427 cm<sup>-1</sup>, bonding N-H 3552 cm<sup>-1</sup>, and paraffin wax at C-H at 3078 cm<sup>-1</sup>, finger print region at 931, 1029, 1165cm<sup>-1</sup>, and Aromatic C-H stretching, N-H stretching and C=C stretching 1633 cm<sup>-1</sup> of glue) (Fig. 3y) revealed that cotton fiber only with microemulsion 3 succeed in solubilize wax and glue but in cases with ME1, 2 the cotton fiber isn't active in solubilize paraffin wax. And according to saw dust Fig.3z revealed that the three microemulsion with saw dust succeed in solubilize of animal glue and paraffin wax.

There is only one note that the Cotton fiber isn't

good enough as the paper pulp and the sawdust in application of the microemulsions on the surfaces although the sawdust turned into powder after dryness so the paper pulp is the most successful one.

### 4. CONCLUSION

The experimental results indicate that the three microemulsions are effective in the solubilization and removal of organic materials, such as animal glue and wax from the painted surfaces. This has been confirmed by FTIR analysis after presented new ways for using microemulsions in cleaning painted surfaces. The first way was about preparing compresses from three different local pulps such as the paper pulp, cotton fiber and the sawdust. The most effective pulp is the paper pulps then the saw dust as FTIR analysis show that the two pulps were effective in solubilizing the glue and the wax. On other hand, the saw dust after dryness turned in to powder. And the direct use of microemulsions by cotton swab on the painted surfaces was very effective in removing the undesired layers in only five minutes, but must be used carefully and under control.

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