Effectiveness Evaluation of Molisch's Test for the Identification of Historical Cellulose Plastics

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Abstract: As is well known, accurate identification of plastics is essential to ensure its future conservation. This is the case, especially, of the cellulose derivatives plastics (cellulose nitrate and acetate) given that both plastics have critical conservation. In addition, each of them requires specific and different environmental parameters, which also involves the differentiation between both, to ensure their permanence. A wipe method called Molisch's Test -usually used to detect cellulose- can be used to identify modified cellulose plastics such as cellulose nitrate and acetate. Although currently there are many analytical techniques that allow us to identify this type of semi-synthetic plastics, they are not always accessible for the collectors and conservators. Therefore, this identification test is very used in this context, as it is very simple and reachable. According to it -and depending on its color results- each plastic can be differentiated since it the produce singular reaction products. However, these molding plastics were often manufactured using fillers in order to modify the qualities of the polymer mixture (color, weight, opacity, among others). These fillers may also include cellulose compounds such as wood flour, paper, and cotton, which can also give equivocal positive results. This research focuses on the effectiveness evaluation of this test, using eleven case studies of identification of historical cellulose plastics using Molisch's test and ATR-FTIR spectroscopy. Thus, the

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differences in coloration obtained with each type of plastic are evaluated and compared with other results obtained with other historical plastics with cellulose fillers. Possible interferences and equivocal positives that may be produced by certain components of the polymer mixture are also evaluated.

Keywords: *Cellulose nitrate, cellulose acetate, Molisch Test, Identification, Polymer, Plastic*

1 Introduction

As is well known, both nitrate and cellulose acetate are two molding plastics of great industrial importance during the second half of the 19th century and the first of the 20th century. Therefore, many objects of both plastics are integrated into artistic, technological and historical collections in recent centuries. However, despite its widespread use, few of them have arrived until today without showing advanced signs of deterioration, since both molding plastics show inherent conservation problems.

In the case of cellulose nitrate, it is susceptible to hydrolysis, thermal and photochemical degradation (Selwitz 1988, 15) being its degradation autocatalytic (Shashoua 2006, 211). It turns yellow and brittle with moderate daylight exposure or if stored at elevated temperatures. The high flammability of the material must be also taken into account (Williams 1994). In its degradation, very reactive and toxic nitrogen oxides are formed, which can react with moisture forming nitric acid (Stewart et al. 1995). It poses a significant risk to the objects stored in its vicinity or on metallic elements (Green and Bradley, 1992). The acidity generated in this process accelerates the reaction, leading to the formation of more acid, which can cause excision of the polymer's main chain so that the material becomes brittle. The most common mechanical damages also include cracking or migration of camphor plasticizers $C_{10}H_{16}O$ (Selwitz 1988, 43) that will sometimes lead to dimensional changes.

In the case of cellulose acetate, it should be noted that it is produced by cellulose acetylation, resulting in diacetate (usually used for molding three-dimensional pieces) or cellulose triacetate (films and fibers) (Reilly

1999). Both versions of the material present severe conservation problems. Thus, objects severely damaged by the hydrolysis that accompany the deacetylation process are common, which results in the emergence of cracks, decays and serious material losses (Price et al. 2008).

Acetic acid is released in the presence of moisture that will catalyze other hydrolytic degradation reactions; this so-called “vinegar syndrome" can cause corrosion of metals or catalyze the degradation of adjacent papers and tissues (Williams, 2002). Normally this phenomenon is accompanied by the formation of surface bloom or cracking. In the final stage of this process, complete deacetylation occurs, resulting in a material chemically similar to cellulose and with similar properties (Shashoua 2008, 182-183).

Likewise, cellulose acetate plastics generally contain a large proportion of plasticizer (esters of phosphoric acid such as triphenyl phosphate or dimethyl phthalate) (Shashoua 2008, 180-1) that migrates easily to the surface, forming a whitish bloom; if it evaporates it can eventually cause deformations, ruptures, and cracks.

Given the need to adapt the environmental conditions to the particular conservation of both plastics, it is necessary to start from a correct material identification. In practice, the identification of historical plastics must be addressed by combining different procedures and based on historical and technological knowledge of them (García Fernández-Villa, De la Roja, and San Andrés 2009). It should include a general delimitation of its possible composition based on the historical study of the piece and its general distinctive elements (color, opacity, signs of degradation, molding, commercial or patent marks, among others) (G. Fernández-Villa, San Andrés and De la Roja 2010). This prior delimitation is essential before addressing the different analysis or tests, including the Molisch Test.

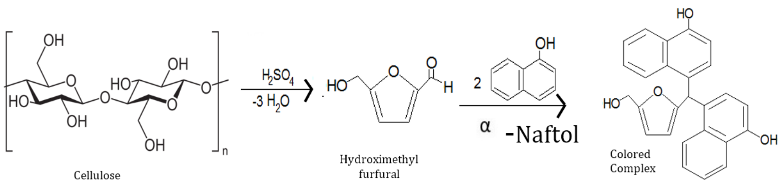


Figure 1: Molisch's reaction

2 Background and Analysis

2.1 Molisch's Test

Molisch's test is a general test for the identification of carbohydrates (monosaccharides, disaccharides, and polysaccharides) described by Hans Molisch (Foulger 1931), an Austrian botanist. Polysaccharides such as cellulose are hydrolyzed to monosaccharides by strong mineral acids (sulphuric acid), and D-glucose monosaccharides formed are then dehydrated to 5- hydroxymethyl furfural; this aldehyde is very reactive and condenses with -naphtol giving a purple or violet colored product (Fig. 1).

In the field of plastics conservation, this test has been used since the mid-60s (Saunders 1966, 21) to identify modified cellulose plastics such as cellulose nitrate and cellulose acetate. Depending on its color results, each one can be differentiated: green for cellulose nitrate and purple or violet for cellulose acetate (Rémillard 2007, 17-18).

2.2 Selected historical plastic objects

For this research, eleven historical plastics objects that could include cellulose nitrate and acetate have been studied, as well as other plastics formulated with cellulosic fillers. These pieces of the 19th-20th century come from different private and institutional collections. The selection has taken into account a previous delimitation, which considers data such as molding marks, trademarks, chronology, smell, weight or opacity, among others (Table 1). Below are the data of each of the selected objects:

Table 1: Details of the historical plastic objects selected for this research

Object	Description	Dimensions (L)x(W)x(H)	Weight
1 	Pincushion	115x74x28 mm	34 g
Remarks: Ivory-like pincushion, from the beginning of the 20th century.It shows yellowing, small dark spots and distorted parallel lines that evidence a probable thermoforming molding.			
2 	Fan	285x170x24 mm	36g
Remarks: Fan punched and decorated with painted flowers, circa 1900. The sticks show significant deformation and general yellowing. It also has several small brown spots.			
3 	Powder Box	115x115x60 mm	42g
Remarks: Ivory-like powder box, circa 1900 from the United States. It shows some dark spots and significant darkening in the inner zone. The exterior has also yellowed and shows the peculiar distorted lines caused by thermoforming molding.			
4 	Toy	111x80x52 mm	42g
Remarks: Red toy manufactured circa 1930-40, marked with "Made in England". It is in good condition. Composed of two halves glued, each part has been injection molded.			

5		Eyeglasses frame	160x142x45 mm	56g	Remarks: Eyeglasses frame of translucent and mottled thermoplastic, spanish origin, probably from the 70s. The pins and the arch show relevant white bloom, probably caused by plasticizer exudation.
6		Film negative fragment	120x16 mm	0,37g	Remarks: 16 mm film from the Conservation and Restoration Center of Spanish Film Library (CCR). It has a strong smell of vinegar and some distortions
7		Child cloth Hanger	140x300x7 mm	35g	Remarks: Child cloth hanger, mid-20th century, from Great Britain. It shows the typical injection-molding marks and the inscription “Made in England”. In good condition, although with some cracking and superficial dirt.
8		Plate	130x130x15 mm	49g	Remarks: Small thermosetting plastic plate, shows a characteristic mottled finish that resembles marble in red, orange and black tones. It shows the marks: “Bandalasta Ware. RECD 187. Made in England”.
9		Plaque	110x110x5mm	119g	Remarks: Plaque of Albert Prince, Queen’s Victoria consort, from the 1863 England Universal Exhibition. Marked at the back “Bois Durci”. Back in very good condition althought the front side shows significant shine loose.

10 	Bowl	110x200x95 mm	315 g
Remarks: A bowl of thermosetting plastic, circa 1950, from the United States. It features a characteristic confetti appearance and is marked at the bottom: "Texas Ware Plastics Manufacturing Co. Dallas Texas". In very good condition, it only shows some minor scratches.			
11 	Camera Baby Brownie	68x79x74mm	195 g

2.3 Experimental

For the Molisch's Test, the followed procedure begins with the preparation of the Molisch reagent, which consists of a 2% concentration solution of (w/v) 1-naphthol in ethanol. Then, a minimum sample of the plastic is taken (for example by rubbing the piece on the matte band of the glass object holder) and then a drop of prepared reagent is added. When ethanol is evaporated, a drop of concentrated sulphuric acid is added (Figure 2).

To verify the effectiveness of the test, their results have been compared with the ART-FTIR spectra. For this, FTIR spectroscopy in mode ATR was used using a Thermo Nicolet 380 spectrometer with a DTGS/KBr detector in the range of 400-4000 nm, spectral acquisition: absorbance mode from 64 scans at 4 cm^{-1} (Figure 3).

The procedure described – both by Molisch test and ATR-FTIR - has been performed on the eleven samples of selected historical plastics. Additionally, both processes have been carried out on cellulose patterns that have been generally used as fillers on historical plastic manufacture (cardboard, wood and paper) in order to know the possible interference that they could have on the result of the coloring tests.

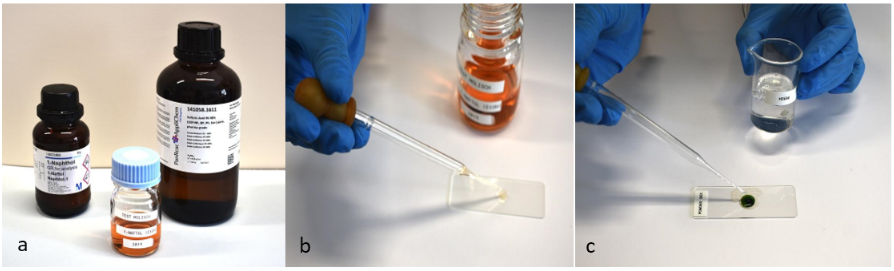


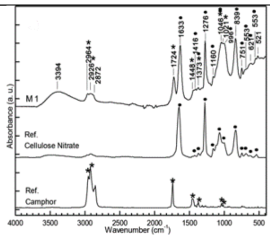
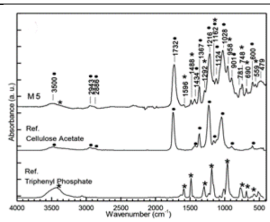
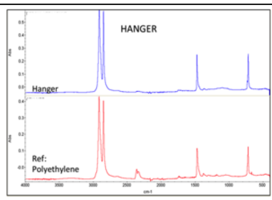
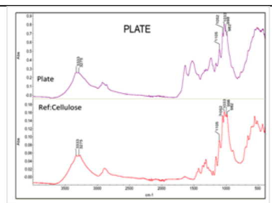
Figure 2: Molisch's test: reactives, sulphuric acid and 2% -naphtol in ethanol (a) and steps of procedure of application (b and c)

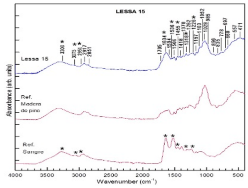
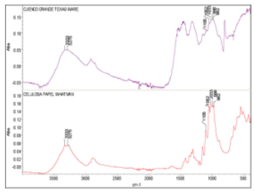
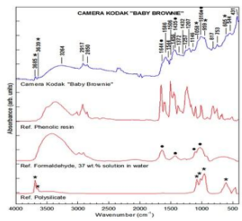
Figure 3: ATR-FTIR analysis on one of the historical plastic objects

3 Results

The results obtained in the Molisch Test and the ATR-FTIR analysis are shown in the following tables, referring to the samples of plastic objects (Table 2) and the possible cellulosic fillers (Table 3):

Table 2: Comparison of the results obtained between Molisch's Test and ATR-FTIR on the historical plastic objects

Object	FTIR-ATR	Molisch's Test	Similar Results
2 			 
4 			 
7 			
8 			

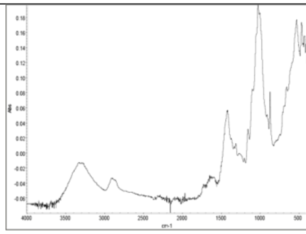
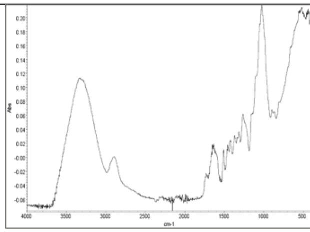
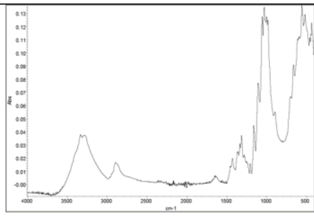
9 			
10 			
11 			

4 Conclusions

The samples identified in ATR-FTIR as cellulose nitrate (samples 1, 2 and 3) show in the Molisch's Test a characteristic and well-differentiated green color. On the other hand, the samples with ATR-FTIR spectra attributable to cellulose acetate (4, 5 and 6) show in the test a purple color, which allows to clearly differentiate between both cellulosic derivatives. In the case of plastics that do not have cellulose in their composition - neither as a polymer matrix nor as a filler (sample 7, with an ATR-FTIR spectrum referable to polyethylene)- no coloration is obtained.

As can be seen, equivocal interpretation may be provided if certain components of the polymer mixture are present, giving a purple color. This is the case, for example, of plastics with cellulose fillers used in the manufacture used in tableware such as urea and thiourea formaldehyde (plate, object number 8) and melamine-formaldehyde (bowl, sam-

Table 3: Results obtained on the reference samples (cellulose fillers) by Molisch's Test and ATR$_{F}TIR$

Reference Sample	ATR-FTIR	Molisch's Test
Cardboard		
Wood		
Paper		

ple 10). Other plastics were usually formulated with sawdust filler, such as bois durci (plaque, sample 9) or compression molding bakelite (Baby Brownie, sample 11), giving the same dark purple color that can be observed on the cellulose fillers analyzed (table 3).

Therefore, it can be concluded that the Molisch's Test is useful and effective in the identification of nitrate and cellulose acetate and that it allows specific identification between them. However, it is essential to perform the previous general delimitation already mentioned in order not to misinterpret positive results that are actually due to the presence of cellulosic fillers.

Declaration of interest

The authors report no conflicts of interest. The authors alone are responsible for the content and writing of this article.

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References

Foulger, John H. 1931. "The user of the Molisch (-Naphthol) reactions in the study of sugars in biological fluids". *Journal of Biological Chemistry* 92: 345–353.

García Fernández-Villa, Silvia, San Andrés, Margarita, and De la Roja, José Manuel. 2010. "Conservar el diseño industrial contemporáneo: problemas prácticos en la identificación de piezas de plástico". In *Conservación de Arte*

Contemporáneo. 11ª Jornada, 331-358. Madrid: Museo Nacional Centro de Arte Reina Sofía.

García Fernández-Villa, Silvia, De la Roja, José Manuel, and San Andrés, Margarita. 2009. "Practical approach to the identification of historical semi-synthetic plastics by ATR-FTIR". In *Technart 2009: Non-destructive and Microanalytical Techniques in Art and Cultural Heritage,* 118. Atenas: Kyriaki Polikreti, Andreas-Germanos Karydas, and Demetrios Anglos, eds.

Green, Lorna, and Bradley, Susan. 1992. "An investigation into the deterioration and stabilization of nitrocellulose in Museum Collections". In *Polymers in Conservation*, edited by Allen, Norman S., Edge, M. D. and Horie, V., 81-96. Cambridge: Royal Society of Chemistry.

Price, Beth A., Malenka, Sally, Sutherland, Ken, Lins, Andrew, and Carlson, J.H. 2008. "Naum Gabo's Construction in Space: Two Cones. History and Materials". In *Proceedings of Plastics: Looking at the Future and Learning from the Past*, edited by Keneghan, Brenda, Betts, Louise, and Louise, Egan. 81-88: London: Archetype and VA Museum.

Reilly, James M. 1999. *Guía del Image Permanence Institute para el almacenamiento de las películas de acetato.* Caracas: Centro Nacional de Conservación de Papel.

Rémillard, France. 2007. "*Identification of Plastics and Elastomers. Miniaturized tests"*. Access in Centre de Conservation du Conservation du Québec: https://www.ccq.gouv.qc.ca/fileadmin/images/img_centre-ress/microtest_ang.pdf.

Saunders, Keith. J. 1966. *The Identification of Plastics Rubbers.* London: Chapman Hall.

Selwitz, Charles. 1988. *Cellulose Nitrate in conservation.* California: The Getty Conservation Institute.

Shashoua, Yvonne. 2006. "Plastics". In *Conservation Science Heritage Materials*, edited by May, Eric and Jones, Mark, 185-210. Cambridge: RSC Publishing.

Shashoua, Yvonne. 2008. *Conservation of Plastics.*Oxford: Butterworth-Heinemann.

Stewart, Robbie, Littlejohn, David, Pethrick, Richard, Tennent, Norman and Quye, Anita. 1995. "Degradation Studies of Cellulose Nitrate Plastics". In *Marble to Chocolate: The Conservation of Modern Sculpture*, edited by Heuman, Jackie, 93-97. London: Archetype Publications Ltd.

Williams, R. Scott. 1994. "Display and storage of museum objects containing cellulose nitrate". *CCI notes 15/3 Canadian Conservation Institute.* https://www.canada.ca/en/conservation-institute/services/conservation-preservation-publications/canadian-conservation-institute-notes/display-storage-objects-cellulose-nitrate.html

Williams, R. Scott. 2002. "Care of Plastics: Malignant plastics". *WAAC (Western Association for Art Conservation) Newsletter*, vol. 24, no. 1: https://cool.conservation-us.org/waac/wn/wn24/wn24-1/wn24-102.html.