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Development of structured natural dyes for use into plastics

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ABSTRACT

This study aimed to identify whether natural dyes encapsulated in a silica matrix via the sol-gel process with the use of alkoxides (as described in INPI patent BR 10 2013 0219835) and subsequently injected into a polyvinyl chloride (PVC) matrix would preserve their original color characteristics after being subjected to Xenon-accelerated weathering (using the ASTM D4452-12 standard). A comparison was conducted of the same natural dyes - carmine, turmeric, indigo and annatto – with and without encapsulation, injected into the same PVC matrix. Color change measurements were made before the weathering test and after 126 h, 252 h, 378 h and 504 h in a Xenon weathering chamber using the ASTM D4459-12 standard. A non-encapsulated Tartrazine dye (INS 102, an azo dye) was used for comparison of the behavior of natural dyes vs. that of synthetic ones. The results pointed to a lack of discoloring protection for the encapsulated natural dyes, which lost saturation more severely than the non-encapsulated ones. It thus follows that some care is required during the encapsulation stages of natural dyes, such as careful dispersion of natural colorants and the inclusion of repeat stages for the encapsulation of the xerogel.

1. Introduction

Color is a paramount contributor to the beauty of nature. It is a major sensory attribute that deeply influences us and is present in a number of items, like fabrics, food, decorative objects and in countless other ways around our environment. It is crucial, for example, for the attractiveness and global acceptance of products such as food [8].

Dyes and pigments are chemical substances or compounds, natural or synthetic, which change the color of another substance or compound when applied to it. Their use has been an activity of economic importance since ancient times, the same consequently being true for the search for new ones. The first dyes were natural, obtained from plants, animals and fungi; the first synthetic dyes, i.e. those made by technological synthesis, would only emerge during the nineteenth century with the development of organic chemistry from fossil sources [2]. The main differences between natural and synthetic dyes are of stability and cost: synthetic dyes are generally more stable and less expensive than natural ones [4].

Despite these advantages, the findings of recent toxicological studies [7], coupled with consumer protection regulations and the associated search for sustainable products that do not have fossil sources, has led to renewed interest in natural dyes that can replace synthetic ones. Such replacements, however, must fall within acceptable parameters of resistance to weathering (especially fading, which is the decrease of saturation by light, especially UV) and be competitive in terms of costs if they are to present a competitive advantage to synthetic dyes.

Taking these aspects into account, this study aims to verify the applicability of the patent registered at the INPI (Brazilian Institute

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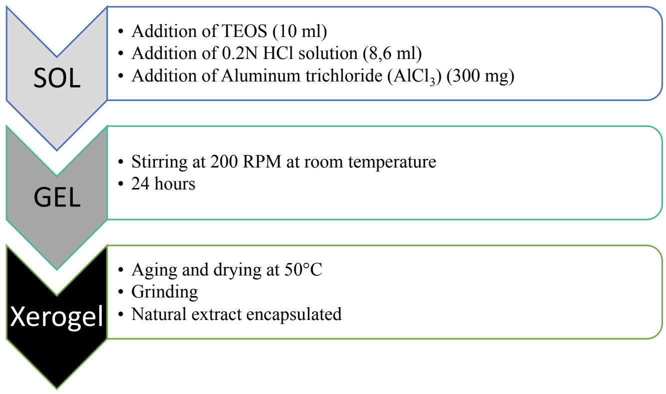

Fig. 1. Flowchart for obtaining natural dyes encapsulated in the silica matrix via the sol-gel process.

of Intellectual Property) under No. BR1020130219835, date of deposit 08/28/2013 under the title: "Structuring Process for Natural Dyes with Hybrid Features Compatible for Application in Polymeric Materials and Cellulosic, Synthetic and Mixed Fibers". The invention describes a process for developing natural dyes with hybrid characteristics (whose product is compatible for use in thermally and mechanically stable polymers and cellulosic and synthetic fibers) that are capable of reproducing the color characteristics of the original natural pigments and present improved performance regarding light fastness and better resistance to several changes when exposed to the weather. The product of the hybrid materials developed can then be applied through simplified processes (with reduced need for inputs, auxiliary products and mordants) on cellulosic, leather and synthetic polymeric materials such as laminates and plastic packages.

This study aims to determine whether the encapsulation proposed for the sol-gel structuring of natural dyes described in the invention in fact minimizes the tint loss-inducing effects of light (i.e. fading or loss of color or saturation). The encapsulation via the sol-gel process uses alkoxides to obtain hybrid (i.e. organic-inorganic) materials, which are then subjected to hydrolysis and condensation reactions through a precursor in order to promote the formation of colloidal-size particles (sol) and subsequent formation of a three-dimensional network (gel).

The sol-gel process is a method applied to the preparation of materials that is based on the polymerization - at room or low temperatures - of simple inorganic compounds. It opened a new field in materials science, focused on macromolecular chemistry [1].

The natural dyes chosen were selected based on the previous experiments that led to the registration of the patent. In them, the best responses to color migration assays for Polyvinyl Chloride (PVC) (ISO 15701:1998) were obtained from the following dyes: indigo carmine (*Indigofera*, blue), carmine cochineal (*Dactylopius coccus*, pink) and turmeric (*Curcuma Longa* L., yellow). These assays were performed with the dyes encapsulated with alkoxides in silica matrices. These natural dyes, including annatto (*Bixa Orellana*, red), are also used quite frequently in the market, having prominent commercial value, which in turn also facilitated their use for this study.

The natural dyes encapsulated in the three-dimensional network with silicon alkoxides were initially prepared through grinding and sifting and then injected into a Polyvinyl Chloride (PVC) polymer matrix. After the injection of the specimens, the colorimetric spectra of the samples were measured using the ASTM D 2244-14 standard, after which they were subjected to accelerated weathering tests in a Xenon arc chamber (Xenotest) in compliance with the ASTM D4459-12 standard - which is standard practice for Xenon arc exposure in testing plastics intended for indoor use. The effect of sunlight was simulated with Xenochrome 320 lamps featuring filters that simulate solar radiation as specified by the International Commission on Illumination (CIE). Sample hue was measured with a CIELab colorimeter at the following times: 0 h (start), 126 h, 252 h, 378 h and 504 h (end). Sample colors were measured after the weathering test in the Xenotest chamber in order to accurately assess the loss of saturation/hue and/or fading said test caused in the colors of the specimens.

This study aimed to identify whether natural dyes encapsulated in a silica matrix by the sol-gel process with the use of alkoxides (as described in INPI patent BR 10 2013 0219835) and subsequently injected into a polyvinyl chloride (PVC) matrix would preserve their original color characteristics after being subjected to accelerated weathering. A comparison was conducted of the same natural dyes with and without encapsulation and injected into the same PVC matrix. A Tartrazine dye (INS 102, an azo dye) without encapsulation was used for comparison of the behavior of natural dyes vs. that of synthetic ones.

There is a promising future for the use of natural dyes in the near future, especially due to the reduced environmental impacts (such as carbon footprint) they represent for the plastic products in which they are used. The use of Life Cycle Assessment (LCA) for products is already a reality in some markets, especially European

Table 2
Xenon-Arc Accelerated weathering test parameters.

Xenon-Arc Accelerated weathering	
Equipment used for exposure	Q-Sun Xe-3-HS accelerated weathering chamber, brand Q-Lab, Serial No. 13-0681-47-X3Hs. CR20/340/BSL Radiometer, Serial No. 12-27717-1-340/BSL
Equipment used for color variation evaluation	ASTM D2244-11-compliant Spectrophotometer: BYK Gardner, Spectro-Guide 45/0 Gloss model (Geometry 45 circ./0), Serial No. 036848; CIE L*a*b* Color System. D65 Illuminant e 10° Observer
Lamp type used	Xenon lamp
Total test time	504 h
Start Date	11/21/2015
Standard	ASTM D4459-12
CIELab sample measurement times	0 h, 126 h, 252 h, 378 h and 504 h
Cycle description	504 h of light exposure
Irradiation intensity	0.3 W/m^2/nm at 340 nm
Black panel temperature	55 ± 2 °C
Humidity	50 ± 10%
Filter used	Window BSL
Radiometer used	CR20/340/BSL
Filter usage time at start of test	15,075 h
Filter usage time at test end	15,579 h