Root Cause Analysis of Color Migration in Footwear: A Case Study

by

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Abstract

The phenomena of migration and/or bleeding of colorants are one of the major concerns for the footwear and leather goods industries. The migration/bleeding of the colorants from one component to the other has been observed in many cases that spoil the aesthetics of the product, which in turn leads to economic loss for the industries. In this research article, a typical case of color migration in leather footwear has been studied in depth for root-cause analysis of the migration problem. The leather used in the shoe upper (affected due to migration), the lining fabric, and the adhesive used in making the footwear were characterized by microscopic and spectroscopic techniques. The FTIR-ATR study revealed that the leather was finished with polyurethane-based coating, the lining fabric used was an aromatic polyester and the adhesive was natural rubber-based adhesive. Though the lining fabric was colorfast to rubbing, it released color in all the organic solvents generally used in natural rubber-based adhesive. Migration studies showed that migration of the colorant (black) from the lining material to the leather (white) happened only in the presence of the adhesive. In conclusion, the organic solvent present in the adhesive used in making the footwear was responsible for the color migration from the lining material to the attached leather. Finally, recommendations have also been made to avoid such problems of color migration in products made from a variety of multiple fabrics.

Introduction

The phenomena of migration and/or bleeding of chemicals and colorants are one of the major concerns for the consumer products such as garments, shoes, bags, etc.[1,2] The migration of colorants spoils the aesthetics of the products and therefore faces rejection, which in turn leads to economic loss for the industries.

Footwear and leather goods are such industries that often face the problem of migration and/or bleeding of chemicals[3–5] and colorants[6–8] from one component to the other damaging the physical-mechanical properties and aesthetics of the product. Leather goods are made with leather along with synthetic (polymeric)/ natural (textile) fabrics, adhesives, threads, etc. The migration of dyes, chemicals, residual solvents, and even fatty matter, from one component to another affects the product quality.[7] These chemicals from any of the components of the product may migrate to the adjacent component and sometimes crosses the adjacent component to reach the next component affecting the product quality. This may also lead to false positive or false negative results specifically for restricted chemicals (phthalates, azo dyes) when tested individually in various components of the product. The presence of solvent-soluble matters including adhesives, and environmental conditions like elevated temperature and humidity, are the essential accelerators of migration.[9–11] In a recent research report by Mandal et al., (2022), the migration of phthalate from PVC sole to the leather insole under various environmental conditions has been shown experimentally.[5] Most of the reported literature in this area talks about the problem of migration and its impact on the product. However, very few research reports are available on the migration issues in leather goods and leather-based footwear.

In this typical case of color migration in footwear, the white finished leather used in the "tongue" of the footwear exhibited a bluish stain from the black colored lining. The colorant used in the lining was migrated to the attached leather (white finish) spoiling the aesthetics of the whole footwear. The primary objective of the present study was to understand the root cause of the migration of the colorant in order to find its solution. The present article describes a systematic study of the physicochemical characteristics of the materials used in making the footwear through spectroscopic and microscopic techniques. To study the migration/bleeding and to understand the root cause of migration, experiments were performed under various chemical and environmental conditions.

Experimental

Materials

The leather, lining fabric, and adhesive used in making the original product (the case) were provided for the study by the same industry that faced the problem of color migration in footwear. Figure 1a shows the section of the footwear affected by the migration of colorant, and the fresh samples of the leather and the lining fabric are presented in Figures 1b and 1c. Standard cotton lawn (rubbing)

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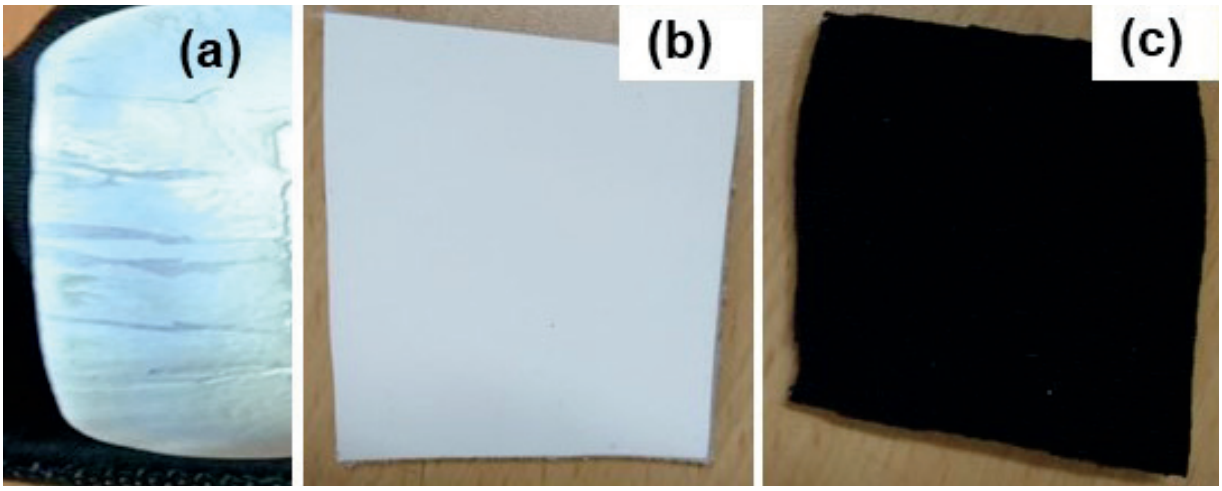

Figure 1. (a) Part of the footwear showing migration of the colorant from the lining material to the white finished leather, and fresh samples of **(b)** the finished leather (white), and **(c)** the lining fabric (black).

fabric (5 cm × 5 cm) complies with ISO 105-F09 was obtained from SDC Enterprises, UK. Standard white pigmented plasticized poly(vinyl chloride) (PVC) sheet (50 mm × 30 mm) complies with ISO150701 / IUF 442 was obtained from James Heal, UK. Solvents used in natural rubber-based adhesive namely, ethyl acetate, toluene, dichloromethane (DCM), tetrahydrofuran (THF), methyl ethyl ketone (MEK), cyclohexane, and acetone[12] were laboratory grade chemicals from Merck, India.

Characterization techniques

Microscopic images of the leather after removing the coating/finishing were captured using a modular stereo microscope model: DZ.5040 from Euromex, Holland. FTIR spectra of the samples were recorded in ATR mode using 4700 ATR-FTIR spectrometer, JASCO, Japan.

The lining material was tested for colorfastness to rubbing by following the test method SATRA TM 167:2017[13] (SATRA TM 167:2017, Color fastness to rubbing – Crockmeter test, SATRA Technology Centre, UK). Here, the test sample was rubbed against a standard cotton lawn in a crock meter (10 times) in dry and wet conditions. After rubbing, the test sample and standard rubbing fabric (cotton lawn) were graded as per grey scale rating on a scale of 1-5. Test for colorfastness to migration was performed by following the standard test method ISO 15701 IULTCS/IUF 442 (Leather — Tests for color fastness - Color fastness to migration into polymeric material).[14] The primary materials used in making the migration-affected section of the footwear were the leather (white finished), the lining fabric (black), and the adhesive. The experiment for colorfastness to migration was performed with the above-mentioned three materials and with the standard PVC sheet (complies with ISO 150701 / IUF 442). The leather, lining fabric, and the PVC sheet were cut into pieces of dimension 3 × 10 cm. The lining fabric was attached to the leather/PVC sheet with and without the adhesive and kept under controlled temperatures (28±2 and 50±2 °C). The color migration was visually assessed after 2 hours. The color bleeding test of the lining fabric was performed by adding 0.2 g (cut pieces of dimension 2-5 mm) of the lining fabric in 5 ml of the solvent taken in a glass test tube and stirring with a vortex mixer of 2 minutes. The UV-Visible spectra of the solution of the colorant from the lining fabric in various solvents were recorded using UV-visible spectrophotometer, model Cary 300, from Agilent Technologies, USA.

Results and discussion

Microscopic and FTIR-ATR study

The microscopic images of the grain side and cross-section of the leather sample after removing the finishing layer are presented in Figure 2. The microscopic image (Fig. 2a) shows the characteristic grain pattern of cow origin leather.[15] The cross section of the leather sample (Fig. 2b) shows that it is made of closely packed fibrous collagen.

The FTIR-ATR spectra of the leather sample before and after removing the coating/finishing layer, lining fabric, and the adhesive are presented in Figure 3a-d. The FTIR-ATR spectrum of the finished leather sample shows all the peaks corresponding to the water-based polyurethane coating (Figure 3a). The characteristic –NH bond stretching and bending vibrations corresponding to the urethane linkage of the PU are observed at 3325.6 and 1529.3 cm^{-1}, respectively.[16] The characteristic stretching vibrations of the carbonyl (–C=O) group of the urethane linkage appear at 1727.9 cm^{-1}. The absorption bands between 1000-1250 cm^{-1} match well with the water-based polyurethane coating.[17] The C–H symmetric and asymmetric stretching vibrations of CH_2 groups can be observed at 2922.6 and 2855.1 cm^{-1}, respectively. The absorption bands at 1459.8 cm^{-1} and 1372.1 cm^{-1} are due to the CH_2 and CH_3 bending vibrations.

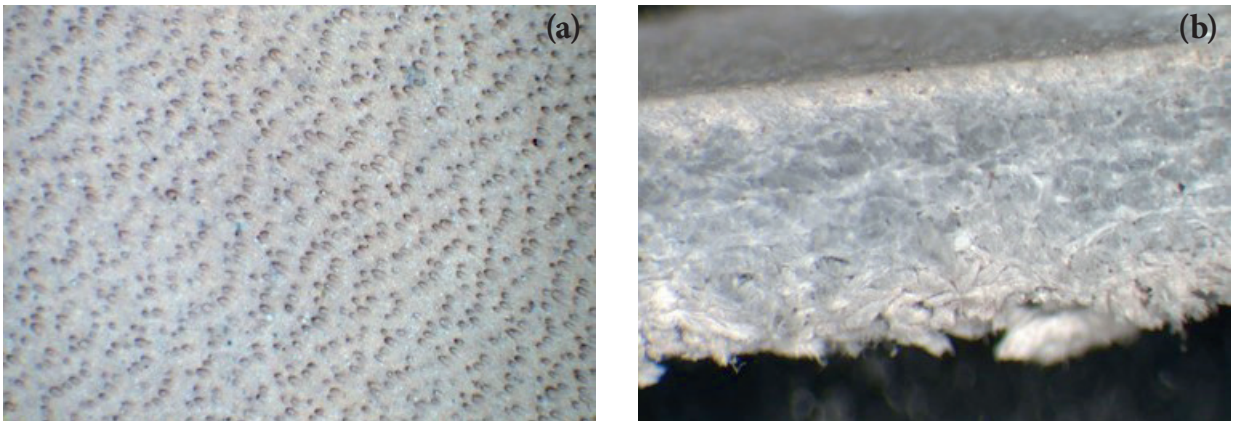

Figure 2. Optical microscopic images of the leather **(a)** grain pattern, 20× magnification and **(b)** cross-section, 40× magnification.

The FTIR-ATR spectrum of the unfinished leather shows distinct peaks characteristic of leather at 1635.3, 1529.3, and 1237.1 cm^{-1} corresponding to the amide I, amide II, and amide III bonds of collagen structure, respectively.[18] The absorption band for amide A of collagen can be seen between 3250-3350 cm^{-1} (Figure 3b).

The FTIR-ATR spectrum of the lining fabric shows that it is made of polyester (Figure 3c). The characteristics bands at 1711.5 cm^{-1} can be assigned to the C=O bond of an ester group. The peaks at 1407.8, 1015.3, and 869.7 cm^{-1} can be attributed to the vibration of aromatic ring.[19] The peak at 1338.3 cm^{-1} is characteristic of -CH_2 groups bending vibration. The peaks at 1239.4 and 967.1 cm^{-1} are due to the characteristic stretching vibration of C-O bond.[19] Peaks at 1463 and 1376 cm^{-1} are identified as C–H bending and C–H deformation of methylene, respectively. The peak at 719 cm^{-1} can be attributed to C-H bending vibrations.[20]

The FTIR-ATR spectrum of the adhesive shows that it is a natural rubber-based adhesive (Figure 3d). The characteristic absorption bands of natural rubber (polyisoprene) are observed at 2955.4, 2944.7, 2866.6, 1660.4, 1449.2, 1375 and at 838.8 cm^{-1} wavenumbers.[21] The strong and sharp absorption band between 2860-2960 cm^{-1} is due the C-H stretching vibrations. The absorption band at 1660.4 cm^{-1} is due to the C=C bond stretching vibrations. The sharp absorption peaks at 1449.2 and 1375 cm^{-1} can be attributed to CH_2 and CH_3 deformation vibrations.[22] The absorption band at 838.8 cm^{-1} is due to the out of plane bending of CH_3 group. Additionally, the broad peak at 3270.7 cm^{-1} due to -OH group indicates that the adhesive used here is hydroxy terminated natural rubber.[23]

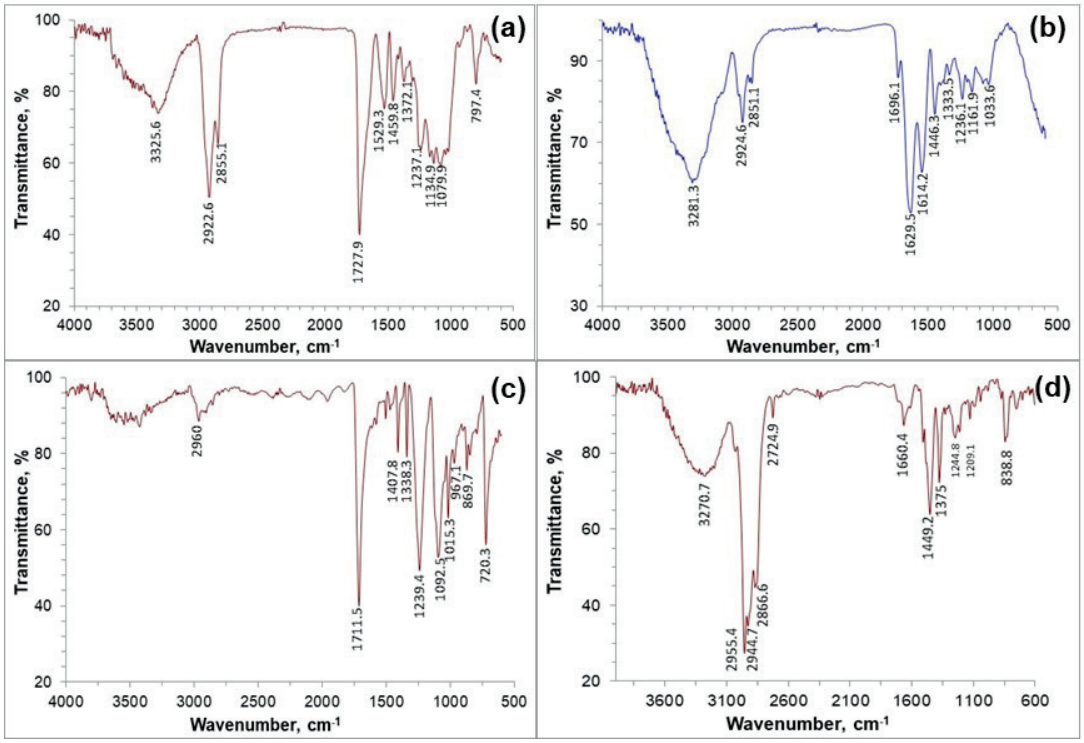

Figure 3. FTIR-ATR spectra of the **(a)** leather sample (as obtained), **(b)** leather sample after removing the finished layer, **(c)** lining fabric, and **(d)** adhesive.

Table I

Values of grey scale rating for the lining and the standard cotton lawn.

Dry rub		Wet rub	
Standard rubbing fabric	Lining sample	Standard rubbing fabric	Lining sample
4/5	4	4/5	4

Color fastness to rubbing of the lining fabric

The lining fabric was tested for color fastness to dry and wet rubbing and the values are presented in Table I. The rub fastness values between 4 and 4/5 for both the lining fabric and the rubbing fabric indicate the lining fabric released very small stain to the rubbing fabric and a very little fading of the color of the lining fabric was observed. This signifies that the lining fabric has very good color fastness to rubbing.

Color migration/bleeding tests of the lining fabric

The migration of the colorant from the lining fabric to the leather and standard PVC sheet when they are kept attached with or without the adhesive has been shown in Figure 4. It can be seen that the colorant is migrated to the attached leather/PVC sheet when they were attached through adhesive. However, no migration of colorant is observed when no adhesive was used between the lining and the leather/PVC sheet. Moreover, it can also be seen that color of the staining on the leather is different from that on the standard PVC sheet.

The leaching out of the colorant from the lining fabric in various solvents used in industrial adhesives are tested. The colorant from the lining fabric is leached out in all the solvents except in water (Figure 5).

The UV-visible spectra of the colorant solutions obtained from the lining fabric in various solvents are shown in Figure 6. The colorant is insoluble in water and the corresponding UV-visible spectrum is overlapped with the abscissa (X-axis) in the whole visible region of the spectrum. The colorant of the lining fabric is highly soluble in all the organic solvents. All the UV-visible spectra of the colorant in organic solvents (except cyclohexane) show that the colorant absorbs the light radiation in the whole visible light wavelength range (390-700 nm) and hence looks black. However, in cyclohexane, the

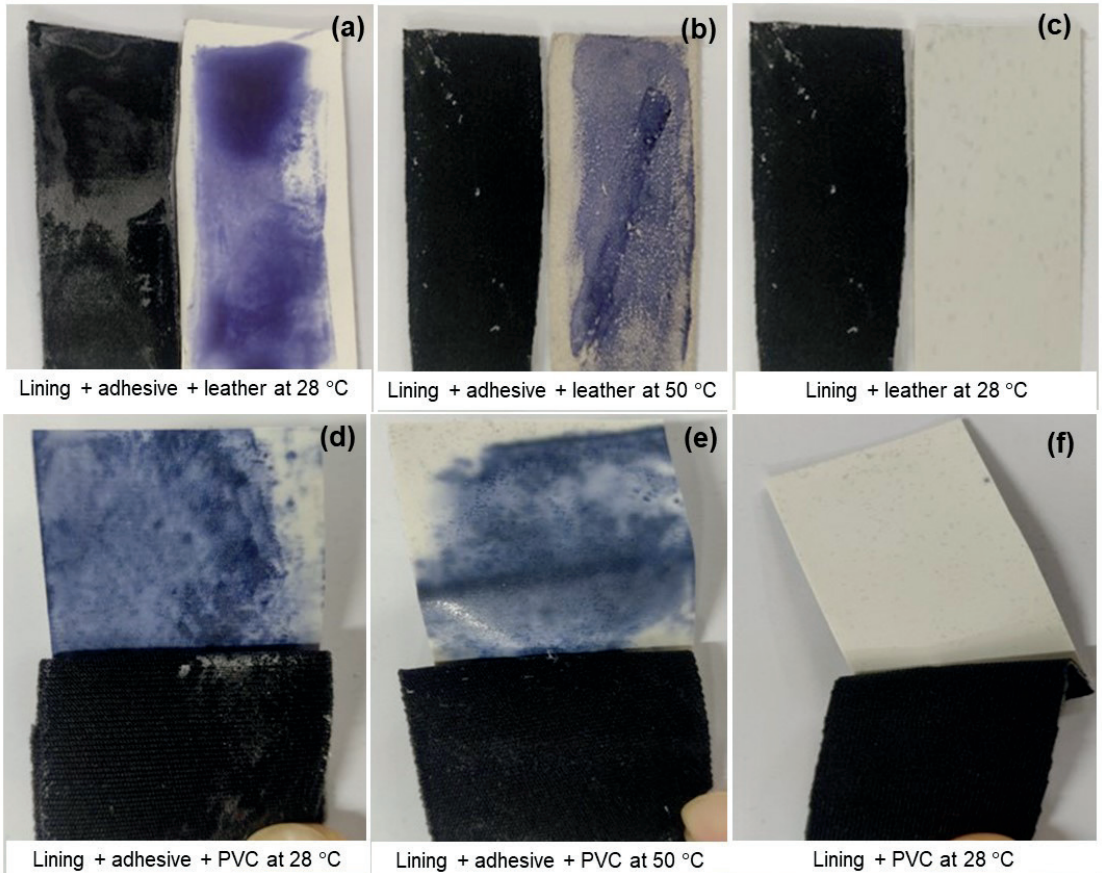

Figure 4. The lining kept attached to the leather **(a, b)** and PVC sheet **(d, e)** using adhesive for 48 hours **(a, d)** at 28°C, **(b, e)** at 50°C, and **(c, f)** lining kept attached to leather/PVC sheet without adhesive for 48 hours.

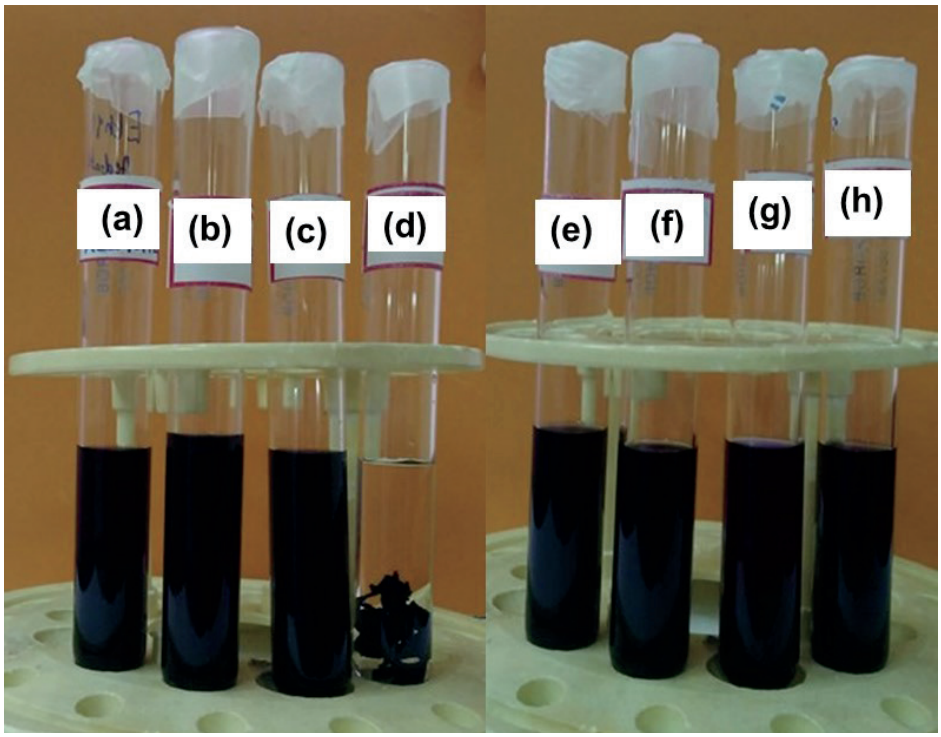

Figure 5. Leaching of the colorant from the lining fabric to various solvents **(a)** Ethyl acetate, **(b)** Toluene, **(c)** Dichloromethane (DCM), **(d)** Water, **(e)** Tetrahydrofuran (THF), **(f)** Methyl ethyl ketone (MEK), **(g)** Cyclohexane, and **(h)** Acetone.

spectrum shows an absorption maximum at 570 nm, which gives a violet coloration. This can be correlated with the color released by the lining fabric to the attached leather shown in Figure 4a-b. This indicates that cyclohexane might have been used as a solvent in the adhesive.

Conclusion

In this specific case of color migration in footwear, the leather, lining fabric and the adhesive used were characterized. The lining material which is a black colored polyester fabric was colorfast to rubbing, however it released color in the organic solvents that are generally used in natural rubber-based adhesives. The adhesive used in this case was identified as organic solvent based hydroxy-terminated natural rubber. Migration studies showed that migration of the color from the lining material to the leather / PVC sheet happened only in the presence of the adhesive. The color migration was very fast and happened within hours even under normal environmental conditions. Therefore, it may be concluded that the organic solvent in the adhesive used in this case was responsible for the color migration from the lining material to the attached leather.

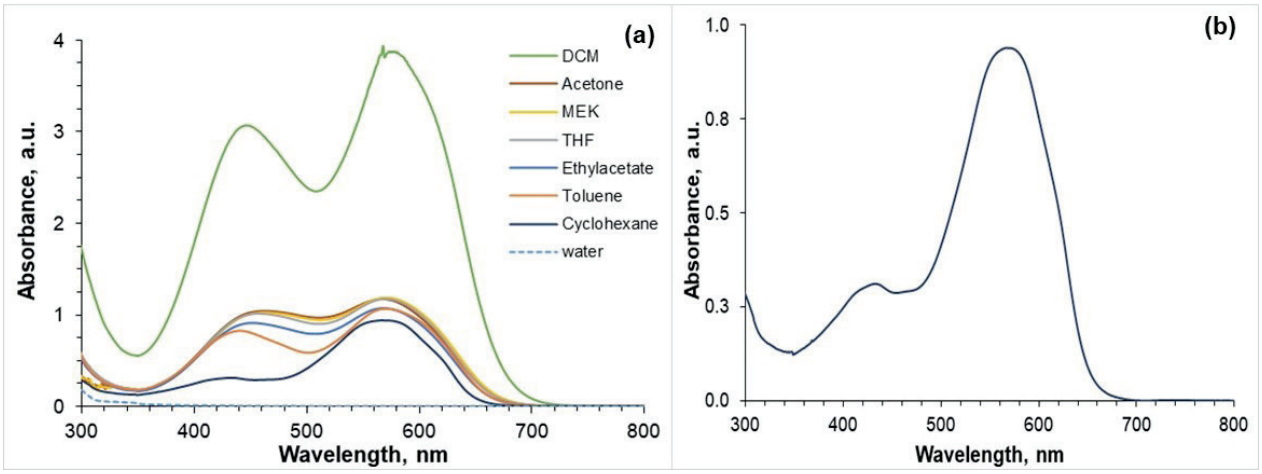

Figure 6. (a) UV-visible spectra of the colorant leached out from the lining fabric in different solvents, and **(b)** projected view of the UV-visible spectrum of the leached-out colorant in cyclohexane.

In the present case of the affected footwear, the colorant from the lining fabric leached-out in the solvent of the adhesive (most probably cyclohexane) and adsorbed on the finished surface of the attached leather. The adsorbed colorant slowly migrated from the edge to the middle of the leather spoiling the aesthetics of the footwear. The solvent in the adhesive is responsible for this migration. Moreover, the solubility of the colorant of lining in the adhesive's solvent contributed to the migration. Therefore, it is recommended to check the solubility of the fabric's colorant in aqueous and non-aqueous solvents, and thereafter select appropriate adhesive to avoid such migration of colorants in products specifically those made from various types of fabrics.

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Conflict of interest

The authors declare that there is no conflict of interest.

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