Testing of the UV light effect on the automotive paints by FTIR spectroscopy

Vodišek, Terezija

Master's thesis / Diplomski rad

2018

Degree Grantor / Ustanova koja je dodijelila akademski / stručni stupanj: **University of Split, University Department for Forensic Sciences / Sveučilište u Splitu, Sveučilišni odjel za forenzične znanosti**

Permanent link / Trajna poveznica: https://urn.nsk.hr/urn:nbn:hr:227:617516

Rights / Prava: In copyright / Zaštićeno autorskim pravom.

Download date / Datum preuzimanja: **2024-03-28**



Repository / Repozitorij:

Repository of University Department for Forensic Sciences

zir.nsk.hr

UNIVERSITY OF SPLIT

dabar
DIGITALNI AKADEMSKI ARHIVI I REPOZITORIJI

UNIVERSITY OF SPLIT

UNIVERSITY DEPARTMENT OF FORENSIC SCIENCES

FORENSIC CHEMISTRY AND MOLECULAR BIOLOGY

MASTER'S THESIS

TESTING OF THE UV LIGHT EFFECT ON THE AUTOMOTIVE PAINTS BY FTIR SPECTROSCOPY

TEREZIJA VODIŠEK

Split, September 2018

UNIVERSITY OF SPLIT

UNIVERSITY DEPARTMENT OF FORENSIC SCIENCES

FORENSIC CHEMISTRY AND MOLECULAR BIOLOGY

MASTER'S THESIS

TESTING OF THE UV LIGHT EFFECT ON THE AUTOMOTIVE PAINTS BY FTIR SPECTROSCOPY

MENTOR: DOC. DR. SC. IVICA LJUBENKOV

CO-MENTOR: DR. SC. IVANA MITAR

TEREZIJA VODIŠEK

356/2016

Split, September, 2018

Thesis was done in Department of Chemistry, Faculty of Science,

University of Split

under supervision of assist. prof. Ivica Ljubenkov

from 01.06.2018 to 13.07.2018.

Date of thesis admission: 13. 09. 2018

Date of thesis acceptance: 17. 09. 2018

Date of defending thesis: 24. 09. 2018

Committee: 1. doc. dr. sc. Željana Bašić

2. dr. sc. Barbara Soldo

3. doc. dr. sc. Ivica Ljubenkov

Table of Contents

Acknowledgment i

Table of Tables ii

Table of Figures ii

1. INTRODUCTION 1

1.1. PAINTS AND PIGMENTS [16] 4

1.1.1. Pigments 7

1.1.2. Solvents 9

1.1.3. Paint additives 9

2. OBJECTIVE OF THE THESIS 10

3. MATERIALS AND METHODS 11

3.1. SAMPLES 11

3.1.1. Yellow pigments 14

3.1.2. Red pigments 14

3.1.3. Blue pigments 15

3.1.4. Green pigments 15

3.2. SAMPLE PREPARATION AND EXPERIMENT 15

4. RESULTS AND DISCUSSION 20

4.1. SPECTROSCOPIC ANALYSIS 20

4.1.1. Italian manufacturer (Happy Color and Eco Service) 20

4.1.2. Croatian manufacturer (Mega akril) 24

4.1.3. German manufacturer (Colors) 27

4.1.4. German manufacturer (Dupli Color) 31

4.2. MICROSCOPIC ANALYSIS 34

4.3. DISCUSSION [40] 37

5. CONCLUSIONS 39

6. REFERENCES 40

7. Abstract 44

CURRICULUM VITAE 46

Acknowledgment

First, I would like to thank my mentor doc. dr. sc. Ivica Ljubenkov for all the help and encouragement in the process of this thesis.

I would also like to thank izv. prof. dr.sc. Dražan Jozić of the Faculty of Chemistry and Technology at University of Split for counselling and cooperation in research.

I am grateful to Department of Chemistry, Faculty of Science and University Department of Forensic Sciences at University of Split for making this research possible.

I am thankful to my family and friends for always being there for me, supported me and showered me with encouragement.

Finally, I am grateful to God. All this could not be possible without Him.

Table of Tables

Table 1 Properties of pigments [16] 8
Table 2 Information about samples 11

Table of Figures

Figure 1 Standard procedure in forensic examination of car paints [3] 1
Figure 2 Electromagnetic spectrum [4] 2
Figure 3 Components of paints [16] 5
Figure 4 Samples at the beginning of the experiment 16
Figure 5 Samples under UV lights. First is series B (304 nm wavelength), second is series C (254 nm wavelength) 16
Figure 6 Adding KBr to the sample and homogenizing material for the pellet 17
Figure 7 Finished pellets of different colours 17
Figure 8 Diagram of FTIR [37] 18
Figure 9 Diagram of Polarized Light Microscope [39] 19
Figure 10 Sample 2, 2A is reference tile, 2B is tile after 30 days under UV light (304 nm) and 2C is a tile after 30 days under second UV light (254 nm) 20
Figure 11 IR spectra of sample 2. The graph at the top represents FTIR spectra of samples under UVB light (304 nm). The second one is FTIR spectra of samples under UVC light (254 nm) 21
Figure 12 Sample 3 after the experiment 22
Figure 13 IR spectra of sample 3 22
Figure 14 IR spectra of a sample 4 23
Figure 15 Tiles of sample 4 24
Figure 16 Sample 7, series A,B and C 24
Figure 17 IR spectra of sample 7. The upper graph is a comparison between obtained spectra in the experiment of series B, below is a comparison for series C 25
Figure 18 IR spectra of sample 8. 26
Figure 19 Tiles of sample 9 26
Figure 20 IR spectra of sample 9 (green). 27

Figure 21 Tiles of sample 12. 27
Figure 22 IR spectra of sample 12. 28
Figure 23 IR spectra of blue sample 13. 29
Figure 24 IR spectra of sample 14 30
Figure 25 IR spectra of sample 15 31
Figure 26 IR spectra of sample 17 32
Figure 27 Tiles of sample 18. 32
Figure 28 IR spectra of sample 18. 33
Figure 29 IR spectra of sample 19 34
Figure 30 Yellow sample under microscope. (a) 15A, (b)15B, (c)15C. 35
Figure 31 Red sample under microscope (a) 17A, (b) 17B, (c) 17C 36
Figure 32 Blue sample under microscope. (a) 8A, (b) 8B, (c) 8C. 36
Figure 33 Green sample under microscope. (a) 4A, (b) 4B, (c) 4C. 37

1. INTRODUCTION

A method of identifying traces of automotive paints with spectroscopic techniques is well established. In this paper we focused not on identifying specific paints, but how exposure to ultraviolet (UV) light effects automotive paints.

Identifying a sample just with infrared (IR) spectroscopic methods does not give sufficient results. The concentration of dyes and pigments is small in paint trace, which makes identification harder. However, this is not a problem for Raman spectroscopy, which is sensitive to small amounts of pigments. IR and Raman spectroscopic methods are complementary and together are interesting tool for forensic automotive paint analysis [1].

The paint coat of automobile is composed of many layers. A new car has about 3-6 layers, a renovated car could have even more than 10 layers. After microscopic properties are determined is time for precise chemical analysis of each layer [2]. Figure 1 shows forensic examination process of car paints.

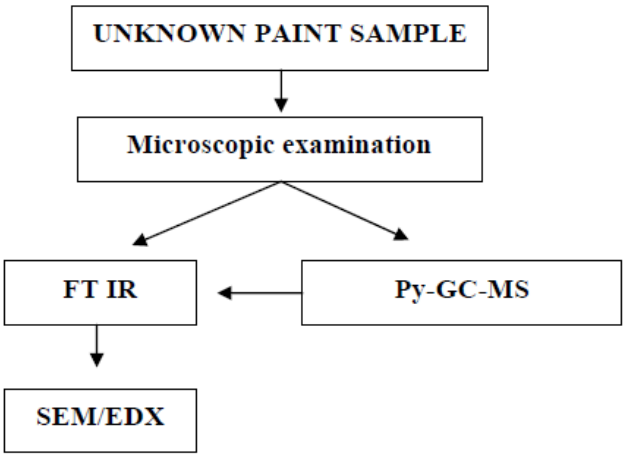


Figure 1 *Standard procedure in forensic examination of car paints [3]*

Part of **microscopic examination** is to determine number, sequence, colour, thickness and texture of layers. Layers are observed on a cross-section of the sample [3].

FTIR (Fourier transform infrared) spectroscopy is very useful for chemical characterization of the sample. Spectroscopy is the study of matter reacting to electromagnetic radiation. Electromagnetic energy can be divided into ultraviolet (UV), visible (VIS) and infrared (IR) region, etc.; and we can divide spectroscopic methods by that as well. As is visible from Figure

2 in IR region (from 700 nm to 10^6 nm) we are dealing with long wavelengths and low energies. This region we can furthermore divide to the near, middle and far IR region. Most used is the middle region (from 2500 nm to 50000 nm or in wavenumbers from 4000 cm^{-1} to 200 cm^{-1}) and this is the one we used in our research.

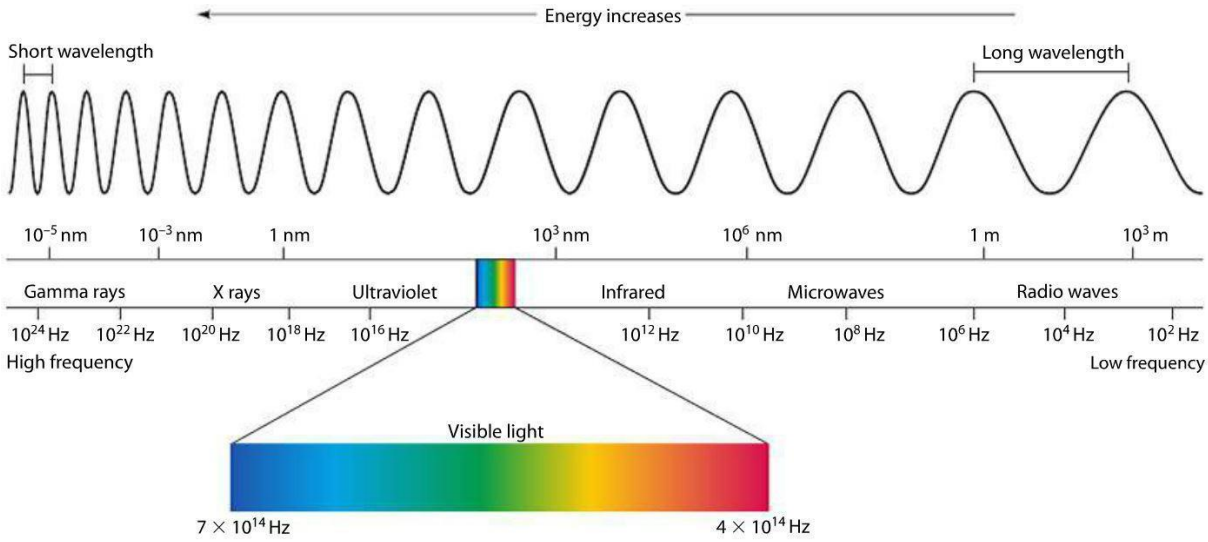


Figure 2 *Electromagnetic spectrum [4]*

Molecules absorb IR radiation when rotation or vibration of the molecule changes dipole moment and the exact amount of energy is provided by the light source. Energy levels for rotations and vibrations are different and are specific for every chemical bond. Vibrations in general, can be placed in two groups, stretching and bending vibrations. Stretching vibrations are movements along the axis of the bond between two atoms. There can be symmetric and asymmetric movement. Bending vibrations are defined by changing the angle between two bonds. There are four types: scissoring, rocking, wagging and twisting. Rotation transitions are important in gases – for every vibrational transition there are several rotation energy levels. However, in solids and liquids rotation is highly restricted and it shows on the IR spectrum only as broadened vibrational band. Although, for IR spectrum to be specific we also need vibrational coupling. The vibrational coupling means that chemical bonds around the one in question influence the energy levels. That way we can discriminate between different functional groups. Moreover, that is why the position of an absorption band corresponding to a given organic functional group cannot be exactly specified [5].

Py-GC-MS (Pyrolysis gas chromatography) is an analytical method in which small amount of organic complex molecules – samples – are broken down by heat to gaseous products and then separated on a chromatographic column and detected in a mass spectrometer [3].

SEM/EDX means Scanning Electron Microscopy and Energy Dispersive X-ray spectrometry. Scanning electron microscopy is used when there is a need for higher magnitude. SEM produces an image with a focused beam of electrons. SEM connected with EDX uses X-ray radiation which is produced when electron beam interacts with the sample for identification of elements in sample. SEM/EDX is non-destructive method and useful when previous analyses are inconclusive[3].

A trace of paint is one of the most common particles examined in forensic investigation. So, it is not surprising that the theme of identifying these traces is well represented in scientific articles. We examined few of them in our research. We could divide them into groups by different methods used in the examination. They used Raman spectroscopy [6-8], combined Raman with IR spectroscopy [9, 10] or added also optical microscopy [11-13]. All these articles present a picture of this important field of forensic sciences.

Chang et al. [14] reviewed the use of automotive paint database. In their opinion forensic examination of car paints involves either comparing a paint chip to a paint sample from a suspected car involved or identification of potential sources with the help of reference collection or database. In the experiment they were checking how the ageing process influence the identification with a database. They left paint samples to the weather conditions for three years. After three years, the searching algorithm still found the nearest match – all changes in the spectrum fell to the "error region" in a search program. Still, ageing effects should be considered when interpreting the searched results.

In one other paper [15] they examined a few environmental factors in which they included mechanical, weathering and biological factors. To our research are the most interesting weathering factors, sunlight to be specific. They stated that the severity of degradation caused by weathering factors strongly depends on climate. However, either way it is almost impossible to prevent automotive paints to be exposed to sunlight. The most harmful part of sunlight is the UV range and most polymers are sensitive to this part of spectra.

1.1. PAINTS AND PIGMENTS [16]

The surface of an object is the most vulnerable. It is open to the air, sun, rain, fog, ice and snow. Because of this iron rusts and wood rots, shrinks or cracks. The everyday object in use are prone to scratches, dents and abrasions. To minimize the damage coatings are applied to the surface. Coatings can also be used to decorate, add colour and smooth the surface. The function of a coating is to protect and to decorate. Wallpapers, plastic sheets, chrome and silver plating can also be called surface coatings in wider sense, but paint is the surface coating which can be applied to any surface, whatever the shape is. The word paint covers all kinds of materials, such as enamels, lacquers, varnishes, undercoats, surfacers, primers, sealers, fillers, etc. All these products are formulated on the same basic principles and contain three main ingredients. First is a pigment. Pigments have a decorative and protective properties. Whitewash is the simplest form of paint, when it is dry it is assembled only of whiting pigment (calcium carbonate – $CaCO_3$). It protects and decorates, but over time it rubs off. The second ingredient helps with that: the film-former also known as the binder. This is a resin or a polymer that bind together the fragments of pigment and hold them on the surface. The third ingredient, solvent, ensures the fluidity of paint, which helps when painting more complex forms. Together the solvent and binder form the base of the paint. When the pigment is not present, the material is called varnish or clear coat when applied over metallic paints. Other names such as enamel, lacquer, finish or topcoat all mean pigmented varnish. Finish or topcoat imply that is the last coat to be applied and also the one that is seen when the object is examined. Thermoplastic solution paints or varnishes are called lacquers – this term is sometimes confusingly used to describe all clear wood finishes. Enamels are usually thermosetting paints with a resemblance to vitreous enamels. Undercoat is a paint applied before topcoat. Some of the undercoats can be defined as fillers or stoppers, primers, surfacers, primer-surfacers and sealers. Fillers or stoppers are used to fill holes and irregularities to provide a level surface for the next coat. Primers promote adhesion and prevent absorption of later coats – they prepare the base material for paint application. Surfacers are called undercoats in decorative house painting are highly pigmented materials. They provide the body of the paint film, level out minor irregularities in the substrate and stick well to primer and topcoat. Primer-surfacers are a combined material which can be used directly on the surface. Sealers are clear or pigmented materials with the function of preventing the passage of substances from one coat to another.

Figure 3 shows a scheme of the composition of paints. Pigments are fine solid particles that do not dissolve in the varnish. When they do not provide colour, they are called extender particles, which are cheaper than prime pigments and can have many other functions, like the improvement of adhesion and film strength. Film-former is a polymer when is dry, but in the wet sample may be the chemical ingredients, partly polymeric, that later react and form the final polymer. The liquid can be separately supplied as a thinner, so the user can adjust the consistency of a paint. Additives are small amounts of substances added for a special jobs.

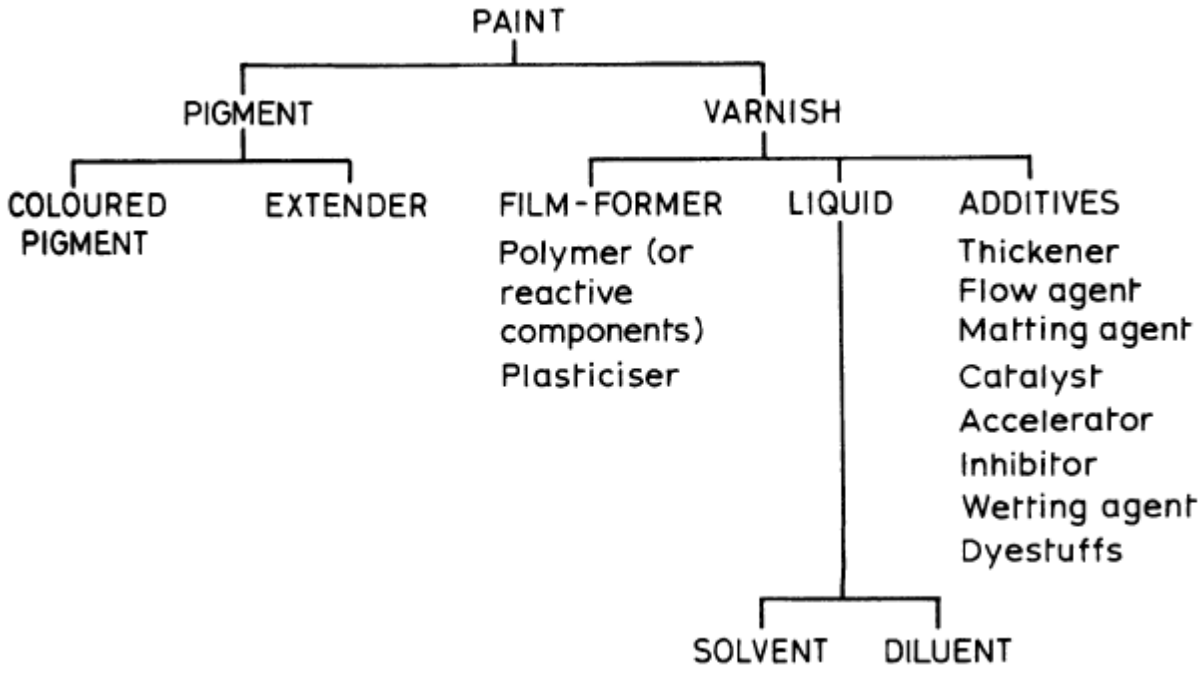


Figure 3 *Components of paints [16]*

The dried paint needs to stick to the surface beneath, be hard and flexible enough for the purpose which is used for and must preserve protective and decorative properties for a long time.

Adhesion has a problem of overcoming a critical face tension. Critical face tension of a smooth solid material is numerical measure of the difficulty of wetting it. To achieve wetting of the surface with paint, surface tension has to be equal or lower than critical face tension. When the surface is wet, molecules in the paint came close enough that forces of attraction between them work and paint stick together.

Hardness, toughness and durability can be achieved with cross-linked films. However, all this can also be accomplished with high molecular weight of linear polymers . The other property, flexibility, often goes against hardness. In cross-linked films they reach flexibility by spacing out the cross-links. To linear polymers they add smaller molecules called plasticizers, which reduce attractive forces between molecules and act as a lubricant, allowing the polymers to slide past one another more easily.

Preserving decorative properties is very important to the users. Gloss can diminish, colour may fade or darken, the surface becomes powdery. All this is a consequence of weathering. Oxygen in the air, water and UV rays all attack paint films, breaking chemical bonds. The surface in time wears away. This could be delayed by the use of resistant polymers and keeping the portion of pigments down. If the volume of pigments in the film is high, then the breakdown of a small amount of polymer cause detachment of surface pigment particles. Fading or darkening of paint can be also delayed by using quality pigments.

The other useful quality of paint is the ease of repairing surface. Objects that are used every day, are prone to scratches and other things that spoil the appearance. If these are small irregularities all that is needed is light abrasion and polishing. For a polish to be great, a surface must be capable of softening by the heat, which will partially flow to even the irregularities. In the cross-linked films this is harder to achieve, but in films constructed of linear polymers it is not that hard.

The process of drying the paint is more complicated than just evaporating of the liquid. There are three mechanisms of drying. First is drying without chemical reaction. In this case drying is solely evaporation of liquids. The polymer is fully formed in wet paint and without solvent is relatively hard and not sticky. There is no chemical change of the polymer during the drying process. Second and third are drying by chemical reaction. Cross-linked polymers are great film-formers, but they are insoluble and cannot be dissolved in solvents. That is why there are linear or lightly branched polymers in the wet paint and then after the paint is applied cross-linking is achieved with chemical reaction. The chemical reaction can occur between ingredients in the paint and the oxygen or water in the air. This then encourage the polymers in the film to cross-link. Alternatively, the chemical reaction is between two ingredients in the paint, which then means that measures must be made to prevent drying of the paint before

it reaches the final destination. This can be achieved by dividing the ingredients into two packs and mixing them just before applying them or choosing ingredients that only react at higher temperatures or exposed to some form of radiation.

1.1.1. Pigments

In a decorative sense the most important part of paint is colour and shine. As discussed before, the pigment gives paints colour. For a matter to be a pigment, it must have some special functions. It must provide colour, special effects (sparkle), must obliterate previous colours, improve the strength and adhesion of the paint film, improve durability, must increase the protection against corrosion, reduce gloss and/or modify flow and application properties. Pigment does not need to have all these functions, but it has to have at least some of them. To choose the best pigment for a specific job we need to know some properties of the pigment. One of them is tinting strength. Tinting strength is sometimes connected with white pigments. Pigment has a poor tinting strength if a lot of it is required to achieve a shade. The tinting strength is independent of its hiding power, that means that relatively transparent pigments can have high tinting strengths.

Lightfastness is another property that we must know. If pigment gives good colour that still is not enough. Colour must last for as long as paint film. Many pigments fade or change shade in the light. This is because sunlight and UV rays break certain chemical bonds and change molecules. Change of molecular structure means different absorption of light in the visible region of the spectrum and consequently different colour. However, if a pigment can absorb UV rays without breakdown, it will protect the binder, and the energy is dissipated as heat. The bleeding characteristic of pigment is something that is not desirable. It got its name after red pigments were dissolved by the white paint and instead of white paint we got pink. This can happen with any colour, but organic reds are very prone to this. On the other hand, high hiding power in something that is much desired. Normally one or two coats of paint should cover any colour. To obliterate pigments must prevent light from passing through the film to the previous layer. Hiding power is described as the number of square meters covered by 1 litre of paint. It depends on wavelengths and total amount of light that pigment will absorb, on its refractive index and particle shape and size.

All pigments are divided as natural or synthetic and organic or inorganic chemicals. In industry today, it is unlikely to find natural organic pigment in use, only synthetic. Contrarily, natural inorganic pigments are still in use and they have a synthetic equivalent. Moreover, although they are chemically the same, they might have different properties. One of the reasons for this is the different shape and size of particles. In controlled conditions, the size of particles can be more uniform, and particles may be induced to take a different shape. The other reason for this are the impurities present in natural pigments. They may contain silica and other impurities which are uneconomical to remove. Despite all the good properties of synthetic pigments, iron oxides are still very important for obtaining red, yellow and black colours.

When we distinguish pigments between organic and inorganic, we can see that organic are far more common now. However, there are ones which contain metallic elements and organic structures. In the Table 1 there are listed pigments properties and preference of the type of pigment used when we want that particular advantage. Although, it may seem that inorganic pigments are more advantageous; organic pigments have a great brilliance and clarity which compensates for other properties.

Table 1 *Properties of pigments [16]*

Property	Preference	Reasons
Brilliance and clarity of hue	Organic	The most attractive, cleanest colours can only be obtained with organic pigments
White and black paints	Inorganic	The purest white pigment is titanium dioxide and black is carbon. There are no organic blacks and whites
Non-bleeding	Inorganic	Inorganic compounds have negligible solubilities in organic solvents
Lightfastness	Inorganic	The valency bonds in inorganic compounds are generally more stable to UV light than in organic compounds.

Property	Preference	Reasons
Heat stability	Inorganic	Very few organic compounds are stable above 300°C.
Anti-corrosive action	Inorganic	All anti-corrosive pigments are inorganic.
UV absorption	Inorganic	Titanium dioxide blocks harmful UV radiation from the binder.
Reflective effects	Inorganic	Aluminium and treated mica available in reflective platelet form.

1.1.2. Solvents

The solvent in the paint industry is used as any liquid that is present or added to paint. The liquids used to dissolve the pigment and binder usually are water, aliphatic hydrocarbon mixtures, terpenes, aromatic carbons, alcohols, esters, ketones, ethers, ether-alcohols, nitroalkanes and chloroalkanes. Properties that are important for liquids in paints are solvency, viscosity or consistency, boiling point and evaporation time, flash point, chemical nature, toxicity, smell and cost. In our case, the drying method was without chemical reaction – just with the evaporation of the solvents we will not go into details about these properties.

1.1.3. Paint additives

Paint additives are added to a paint in amounts as little as 0.001% to 5%, but they have great influence on the physical and chemical properties of the paint. Some additives affecting viscosity are silica and silicates, resinous thickeners and metal chelates. Representative for additives affecting surface and interfacial tensions are surfactants. There are also additives affecting appearance, chemical reaction and living microorganisms.

2. OBJECTIVE OF THE THESIS

The main objective of this research is to determine the effect of UV lights on automotive paints. The other goal is to identify specific pigments used in paints.

We expect that the composition of paint changes when the paint is exposed to UV light over long period of time. We assume that changes can be seen and identified by IR spectra.

3. MATERIALS AND METHODS

Materials we used in this research were automotive spray paints in cans, small stainless-steel tiles and chemicals used for FTIR. We used two UV bands, one with 254 nm and other with 304 nm wavelength. The methodology was IR spectroscopy and the analysis of obtained results.

3.1. SAMPLES

Our research used cost effective spray paints made for repairing coatings on the automobiles. In Table 2 are collected data about samples. Information was gathered from spray cans in which the paints were and safety sheets available online [17]. There was almost no information about the content on the cans. Still, we managed to find some on the safety sheets, but there were no data about used pigments. RAL number is a colour standard given by a German organization Reichs-Ausschuss für Lieferbedingungen for easier specification of colour shades in the market [18].

As is shown in the Table 2 we used spray paints made in Italy, Croatia and Germany. They were all acrylic paints yellow, red, green or blue colour. Specific pigments were determined by comparing the IR spectra of the samples with IR spectra of known pigments. Because there are no official data, our results are the best we could do with the available information.

Table 2 *Information about samples*

Sample No.	**Colour**	**RAL**	**Name**	**Manufacturer**	**Main ingredients**	**Chemicals in traces**
2	yellow	1016	Happy color	SARATOGA INT. SFORZA SPA, Via Edison 76, 20090 Trezzano s/naviglio, Italy	methyl acetate, propane, n-butyl acetate, butane, dimethyl carbonate	isobutane,methanol, 2-butoxyethanol, ethylene glycol, monobutyl ether

Sample No.	Colour	RAL	Name	Manufacturer	Main ingredients	Chemicals in traces
3	blue	5013	Eco Service	ECO SERVICE, Viale Europa 1 - Z.I., 36053 Gambellara, Italy		
4	green	6029	Happy color	SARATOGA INT. SFORZA SPA, Via Edison 76, 20090 Trezzano s/naviglio, Italy	methyl acetate, propane, n-butyl acetate, butane, dimethyl carbonate	isobutane,methanol, 2-butoxyethanol, ethylene glycol, monobutyl ether
7	red		Mega akril	MADEX d.o.o., Zlatka Balokovića 20, 23000 Zadar, Croatia		
8	blue	5013	Mega akril	MADEX d.o.o., Zlatka Balokovića 20, 23000 Zadar, Croatia		
9	green	6005	Mega akril	MADEX d.o.o., Zlatka Balokovića 20, 23000 Zadar, Croatia		
12	red	3000	Colors	MOTIP DUPLI GmbH, Kurt-Vogelsang-Str. 6, D-74855 Hassmersheim, Germany		

Sample No.	Colour	RAL	Name	Manufacturer	Main ingredients	Chemicals in traces
13	blue	5010	Colors	MOTIP DUPLI GmbH, Kurt-Vogelsang-Str. 6, D-74855 Hassmersheim, Germany		
14	green	6005	Colors	MOTIP DUPLI GmbH, Kurt-Vogelsang-Str. 6, D-74855 Hassmersheim, Germany		
15	yellow	1023	Colors	MOTIP DUPLI GmbH, Kurt-Vogelsang-Str. 6, D-74855 Hassmersheim, Germany		
17	red	3020	Dupli-Color Prima	MOTIP DUPLI GmbH, Kurt-Vogelsang-Str. 6, D-74855 Hassmersheim, Germany	acetone, dimethyl ether, n-butyl acetate, propane, butane, 2-metoxy-1-methylethyl acetate	isobutane, cellulose nitrate

Sample No.	Colour	RAL	Name	Manufacturer	Main ingredients	Chemicals in traces
18	blue	5010	Dupli-Color Prima	MOTIP DUPLI GmbH, Kurt-Vogelsang-Str. 6, D-74855 Hassmersheim, Germany	acetone, dimethyl ether, n-butyl acetate, propane, butane, 2-metoxy-1-methylethyl acetate	isobutane, cellulose nitrate
19	green	6005	Dupli-Color Prima	MOTIP DUPLI GmbH, Kurt-Vogelsang-Str. 6, D-74855 Hassmersheim, Germany	acetone, dimethyl ether, n-butyl acetate, propane, butane, 2-methoxy-1-methylethyl acetate	isobutane, cellulose nitrate

3.1.1. Yellow pigments

For sample number 2 we deduced pigment used was yellow iron oxide [19] also known as iron (III) trihydroxide or Pigment yellow 42. Yellow iron is a natural inorganic matter used in paints, enamels, concrete colorants, rubber and paper [20].

The pigment of another yellow sample, sample 15, is one of diarylide pigments [21], pigment yellow 12. This is an organic compound also known as azo compound. This name describes all compounds with functional group R-N=N-R'. In this instance R means aromatic molecules [22].

3.1.2. Red pigments

Sample 7 consist of Pigment red 5 [23], which is one of the organic red pigments. Its whole IUPAC name is N-(5-chloro-2,4-dimethoxyphenyl)-4- [[5-(diethylsulfamoyl)-2-methoxyphenyl] hydrazinylidene] -3-oxonaphthalene-2-carboxamide [24].

In sample 12 we found pigment 220 [25]. It is an organic pigment with the molecular structure of double azo structure.

Sample 17 contained Pigment red 48 [26]. This is also one of the organic red pigments, sodium salt - disodium 4-[(5-chloro-4-methyl-2-sulphonatophenyl)azo]-3-hydroxy-2-naphthoate.

3.1.3. Blue pigments

Pigment blue 60 [27] was found to be a part of samples 3 and 8. It is also called Indanthrene blue. This pigment is an organic dye made from 2 aminoanthraquinone treated with potassium hydroxide [28].

For samples 13 and 18 we deduced that the pigment used was Cobalt blue [29]. It is an inorganic pigment - cobalt aluminate ($Al_2Co_2O_5$) [30].

3.1.4. Green pigments

In sample 4 was used Pigment green 7 [31]. This organic pigment is also known as halogenated copper phthalocyanine or phthalo green [32].

Sample 9 contained Pigment green 10 [33]. This is also organic pigment, one of Nickel complexes.

Sample 14 consisted Pigment green 17 [34] or Chromium (III) oxide. It is inorganic pigment with chemical formula Cr_2O_3. It is found in nature as rare mineral eslolaite [35].

For sample 19 was used Pigment green 36 [36]. This organic pigment is related to Pigment green 7. In this pigment chlorine atoms (which are in Pigment green 7) are replaced with bromine.

3.2. SAMPLE PREPARATION AND EXPERIMENT

On cleaned stainless steel tiles we applied spray paints – three tiles for each colour. Figure 4 presents one set of painted tiles. In this picture there are also black and silver samples, but we excluded them from experiment, because obtaining clean IR spectra for these was much harder than with other colours.



Figure 4 *Samples at the beginning of the experiment*

After securing all the samples we put one set of tiles under 304 nm UV light (series B) and one under 254 nm UV light (series C). One set (series A) we used as reference samples (blanks).

We left series B and C under UV lights first for 15 days and then for 15 days more. In between we obtained IR spectra of reference samples.

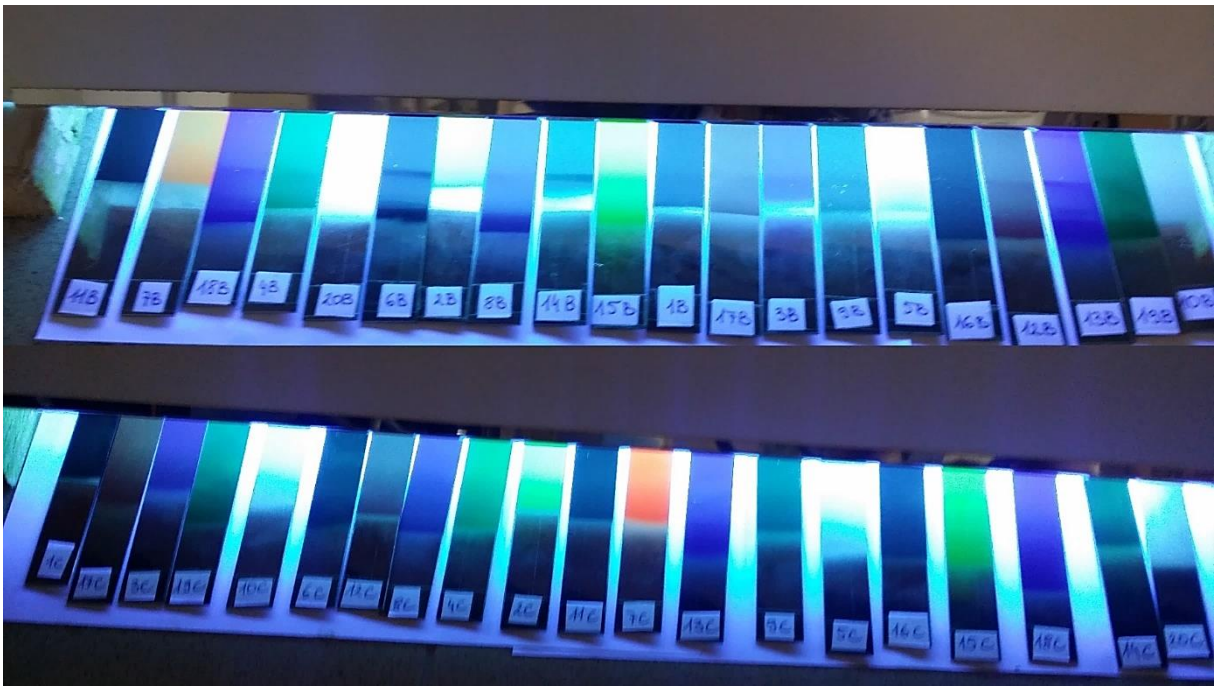


Figure 5 Samples under UV lights. First is series B (304 nm wavelength), second is series C (254 nm wavelength)

The process of obtaining IR spectrum was the same for all samples. First, we scraped a little bit of paint from stainless steel tile. We added potassium bromide (KBr) and made a pellet

(Figure 6). In the process of making pellets/discs, we had to be very careful. The pellet had to be strong enough, so it did not break when put in the measuring cell. It had to have the right quantity of sample – if we put too much of it, the pellet was not transparent enough, if we put too little, we could not detect it. In Figure 7 we can see products of successful tries. KBr was used for making the disc because of its transparency in regions from near ultraviolet to infrared wavelengths and has no significant optical absorption lines in its high transmission region.



Figure 6 *Adding KBr to the sample and homogenizing material for the pellet*

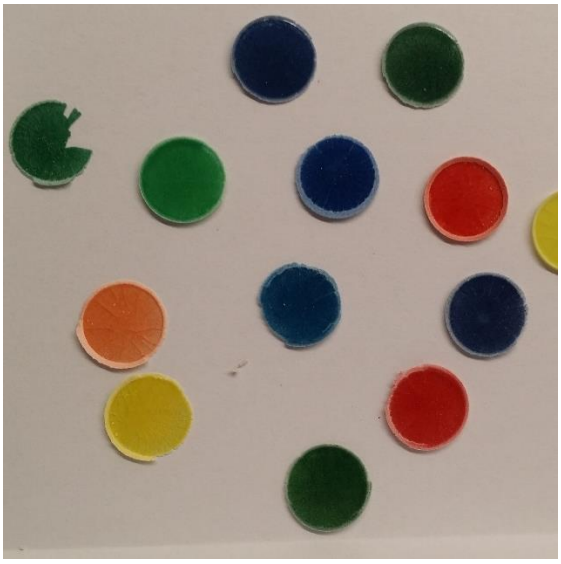


Figure 7 *Finished pellets of different colours*

After we made KBr discs we put them in Fourier Transform Infrared Spectrophotometer (FTIR). We used Shimadzu FTIR – 8400S.

Fourier Transform Infrared Spectrophotometer is composed of the source of IR radiation, wavelength selector, sample cell, detector and signal processor (Figure 8). The FTIR spectrophotometer replaced the dispersive IR spectrometer because the radiant power that reaches detector is much greater, so it is possible to analyse complex spectra and the time to obtain spectrum is considerably shortened. With the FTIR spectrophotometer we get one spectrum in less than 1 s [5]. Figure 8 shows a simplified diagram of the instrument we used for our measurements.

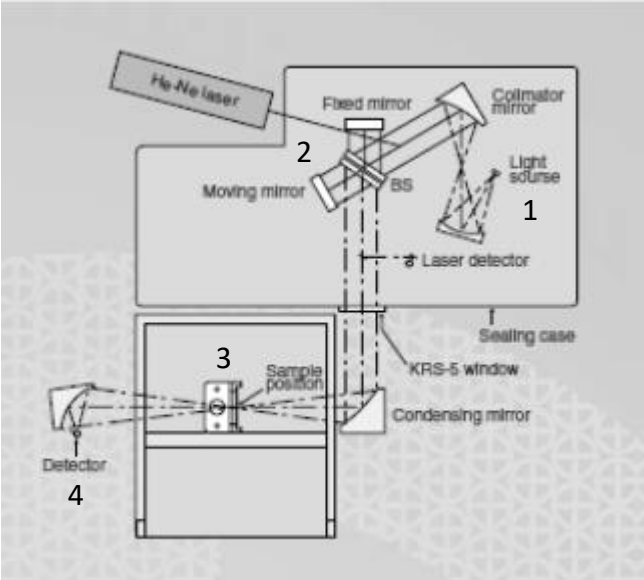


Figure 8 *Diagram of FTIR [37]*

Number 1 on Figure 8 represents light source. Mirrors around number 2 are part of Michelson interferometer. Number 3 is sample compartment and 4 is a detector. The interferometer is one of the most important parts of FTIR. Michelson interferometer consists of 3 mirrors and the beam splitter. After the beam goes past the first mirror it falls on the beam splitter, which divides the beam on the remaining two mirrors of which one is fixed and other is movable. The optical system of FTIR must be sealed because the beam splitter is susceptible to moisture [5].

Before we can obtain a spectrum, we have to choose an apodization function very carefully. We get a spectrum when a Fourier transformation is applied to measured interferogram. However, in reality, a moving mirror cannot move in an infinite range, so ripples are formed around large peaks. Apodization functions help us get a cleaner spectrum. There are a few functions to choose from. Most common are named Box-car, Triangular and Happ-Genzel. Each of these functions give us a different solution to a problem. The Box-car function is used when we need good resolution, the Triangular when we need simple spectrum without large ripples and the Happ-Genzel apodization function is considered to have a good balance between ripple size and resolution [38].

Obtaining a spectrum is easy. First, we initiate the FTIR and connected PC. After waiting a few minutes for the optical system to stabilize we measure the background spectrum. Then we put the sample in sample compartment and measure the spectrum of the sample. The

software (IR Solution) calculates itself and give us a spectrum without background. With the use of software, we can find peaks and calculate area under them.

At the end of the experiment (after 30 days) we examined the tiles under a polarization microscope. We took one set of tiles (tile from series A, series B and series C) for each colour and look for changes between them.

Polarized light microscopy is a technique that improves the quality of the image by contrast-enhancement. Polarized light microscope observes specimens that are visible because of their optically anisotropic character. Because of this, the microscope needs a polarizer, placed in the light path before specimen, and an analyser (a second polarizer) positioned after it. On Figure 9 is a picture of one example of a polarized light microscope [39].

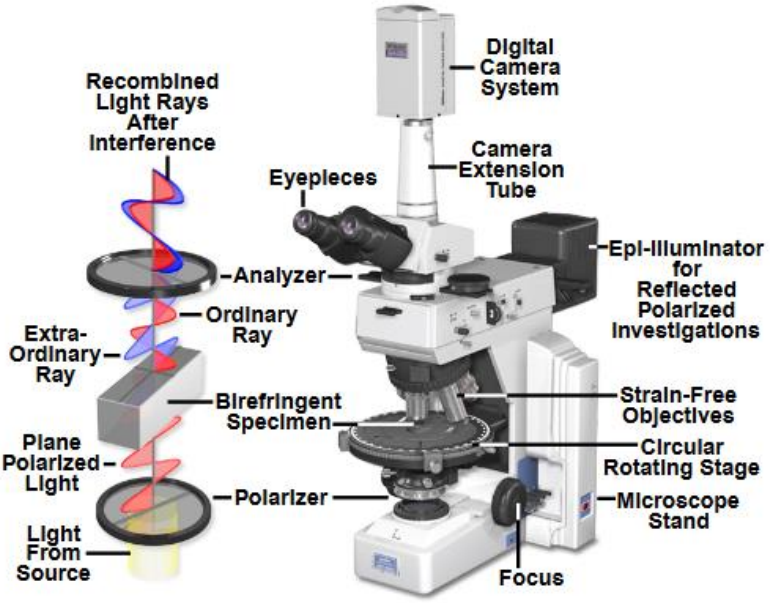


Figure 9 *Diagram of Polarized Light Microscope [39]*

Basically, a polarized light microscope is great for analysing matter that produces two different wave components upon reflection, because we can, with the help from analyzer, see both. Moreover, this can reveal detailed information about structure and composition of materials [39].

For our research we looked at the surface of painted tiles and looked for differences.

4. RESULTS AND DISCUSSION

The results of our experiment were IR spectra and images taken with polarized microscope. In this chapter, we will represent both.

4.1. SPECTROSCOPIC ANALYSIS

As mentioned before, in this research we put painted stainless steel under two different UV bands. On day 15, we sampled the paint and put them back. On day 30 we stopped the experiment. We measured the IR spectra of each sample three times – at the beginning (day 0), the middle (day 15) and at the end (day 30). We arranged samples into groups based on the brand.

4.1.1. Italian manufacturer (Happy Color and Eco Service)

In this group we have yellow (sample 2), blue (sample 3) and green (sample 4) spray paint.

- **Yellow paint**

On Figure 10 we see the state of the tiles after the experiment. Change can be seen with naked eyes.

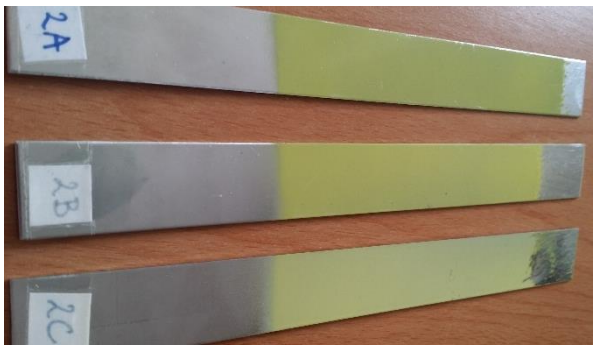


Figure 10 *Sample 2, 2A is reference tile, 2B is tile after 30 days under UV light (304 nm) and 2C is a tile after 30 days under second UV light (254 nm)*

However, if we look at the IR spectra (Figure 11), the change is not that great. The highest peak of reference sample is at 1732 cm^{-1} and this stays the same even after 30 days under UV lights. When we look at the peaks of pigment, we can see that the peak at 998 cm^{-1} disappears in both sets of the experiment. However, this alone cannot explain the fade of the colour we see at Figure 10.

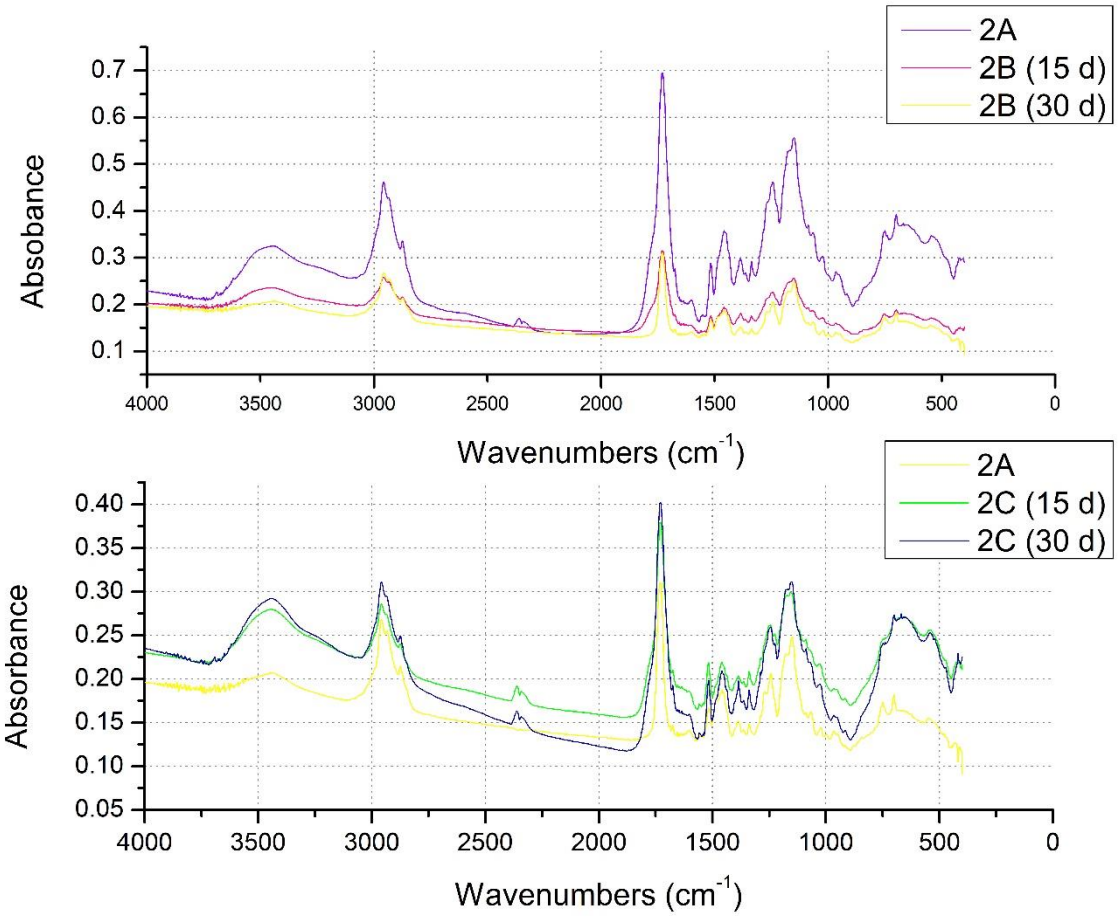


Figure 11 *IR spectra of sample 2. The graph at the top represents FTIR spectra of samples under UVB light (304 nm). The second one is FTIR spectra of samples under UVC light (254 nm)*

- **Blue paint**

In the blue paint, peaks of pigments at the IR spectra (Figure 13) do not change under UV lights after 30 days. There is no noticeable change of IR spectra in series B or in series C.

Same as yellow sample the highest peak is at 1732 cm^{-1}. That is absorption signal of carbonyl group in acryl polymer. The other important group of peaks is around 2900 cm^{-1}.

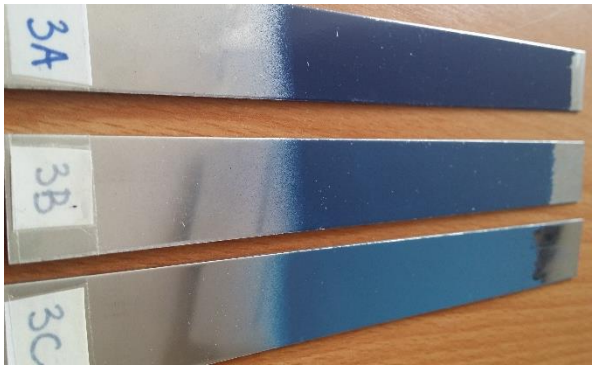


Figure 12 *Sample 3 after the experiment*

Figure 12 shows how tiles look after 30 days of experiment. The colour is visibly changed. We can even distinguish between tile in series B (3B) and tile in the series C (3C).

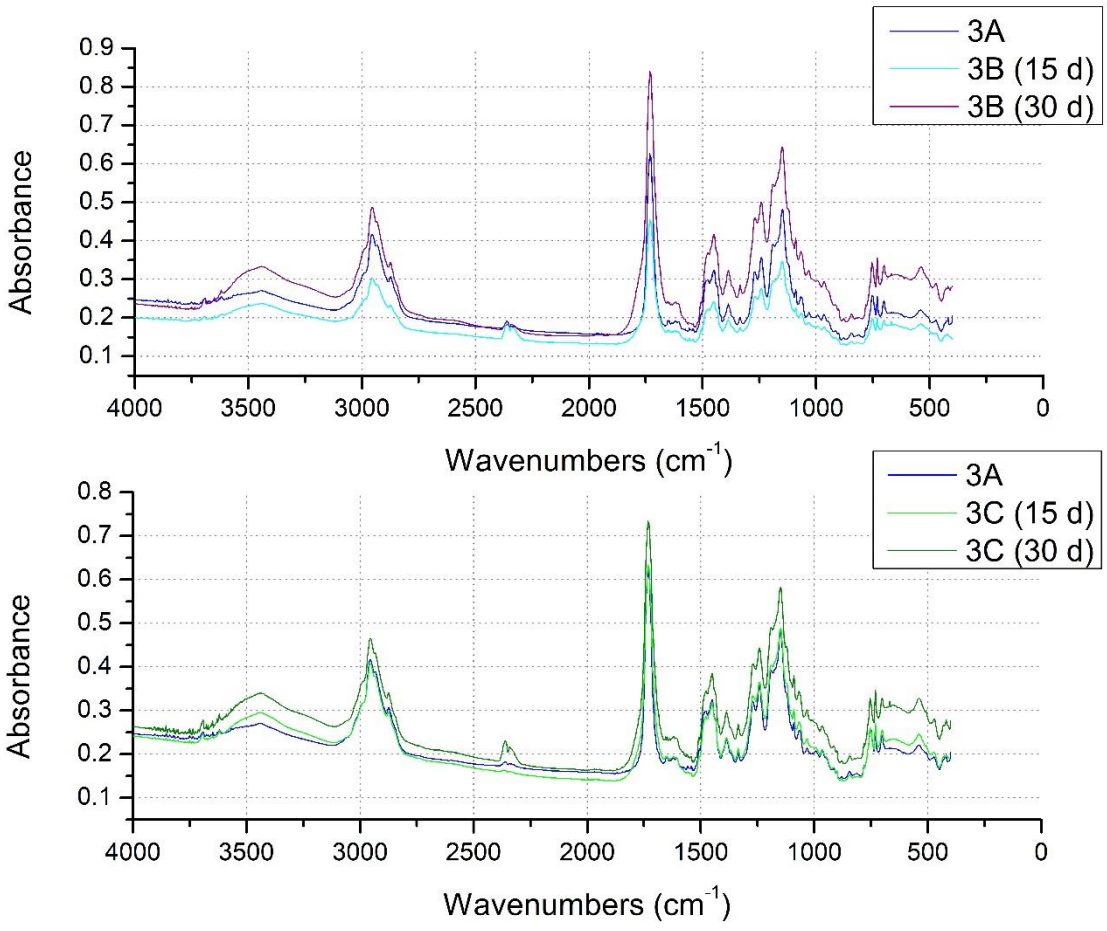


Figure 13 IR spectra of sample 3

- **Green paint**

In green spectra of this manufacturer there are some more changes. If we focus first at the top graph on Figure 14, changes are the same after 15 and 30 days. Peaks at the wavenumbers 1603 and 1673 cm^{-1} disappear from the IR spectrum. In the series C (graph below) peak at 1603 cm^{-1} wavenumber also disappear.

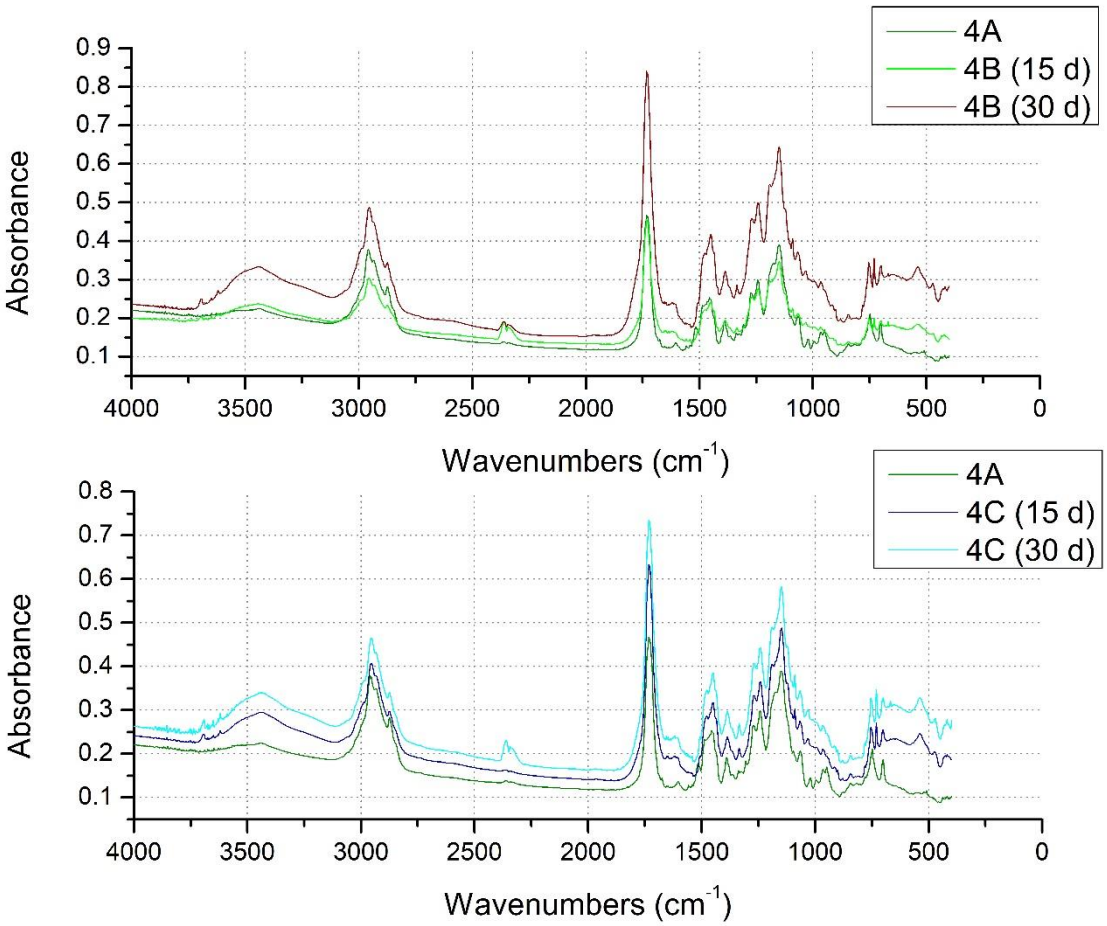


Figure 14 *IR spectra of a sample 4*

Concerning peaks of pigments there are no changes in IR spectrum. How the colour visually changed we can see on Figure 15.



Figure 15 *Tiles of sample 4*

4.1.2. Croatian manufacturer (Mega akril)

This group consist of red (sample 7), blue (sample 8) and green (sample 9) paints.

- **Red paint**



Figure 16 *Sample 7, series A,B and C*

With this sample, change is the most visible (Figure 16). In the experiment of series B, from 8 peaks for a pigment that we identified, only 2 were left. There are many peaks that vanished or appeared in this experiment. The one who appeared had a wavenumbers 616, 790, 1450, 1655 cm^{-1}. There was one who appeared only after 30 day – 1098 cm^{-1}. Peaks which disappeared were at wavenumbers 690 and 875 cm^{-1}. Another interesting thing is shift of a peak. From position at 3400 cm^{-1} went to 3230 cm^{-1}.

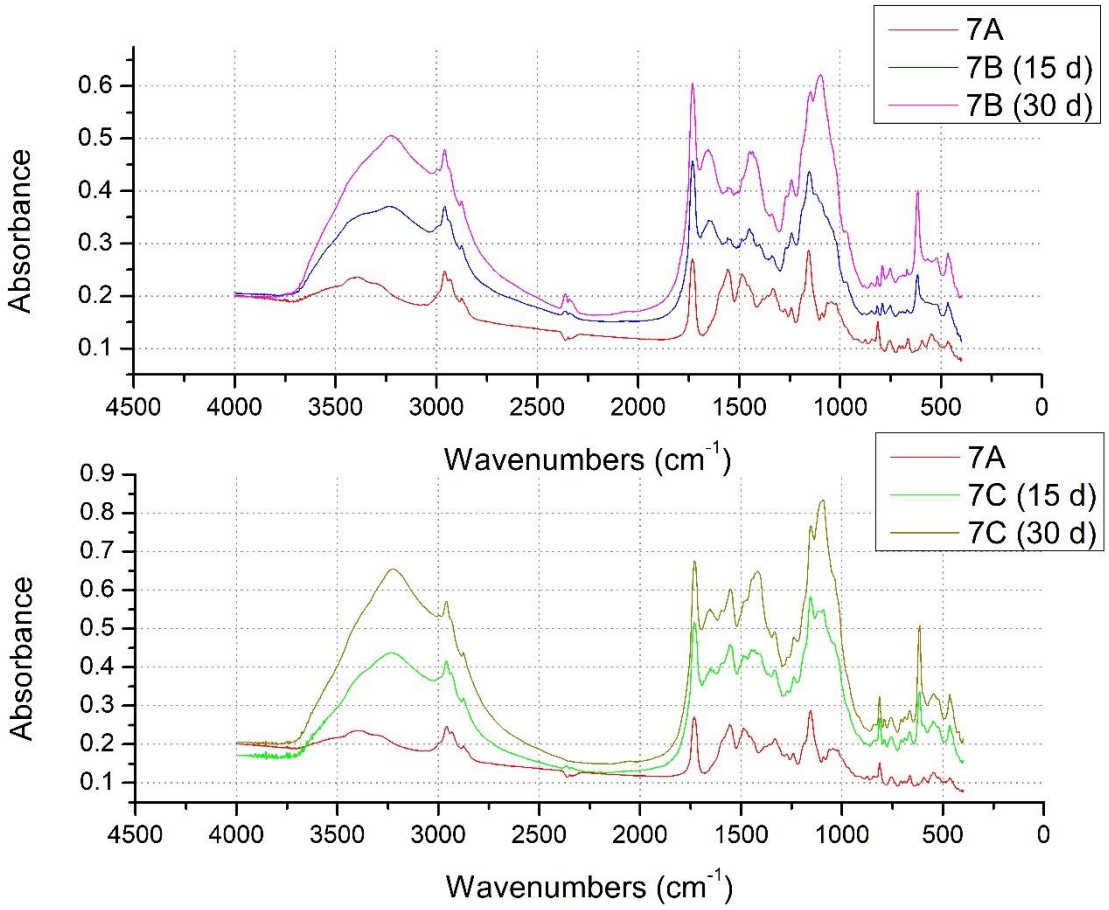


Figure 17 *IR spectra of sample 7. The upper graph is a comparison between obtained spectra in the experiment of series B, below is a comparison for series C*

In the experiment of series C, pigment peaks did not change so much. Only the peak at wavenumber 594 cm^{-1} disappeared. The same shift (from 3400 to 3230 cm^{-1}) did occur. Few peaks were developed (at wavenumbers 617, 1430 and 1655 cm^{-1}) and few disappeared (at 875, 1020, 1045 and 1385 cm^{-1}).

- **Blue paint**

This sample has the same pigment as the blue paint in the group before. Visual change is therefore very similar to Figure 12. In series B peak at wavenumber 670 cm^{-1} vanished. In the experiment with the set C, were even less changes. In Figure 18 we see both graphs. First is for series B and the second one is for series C.

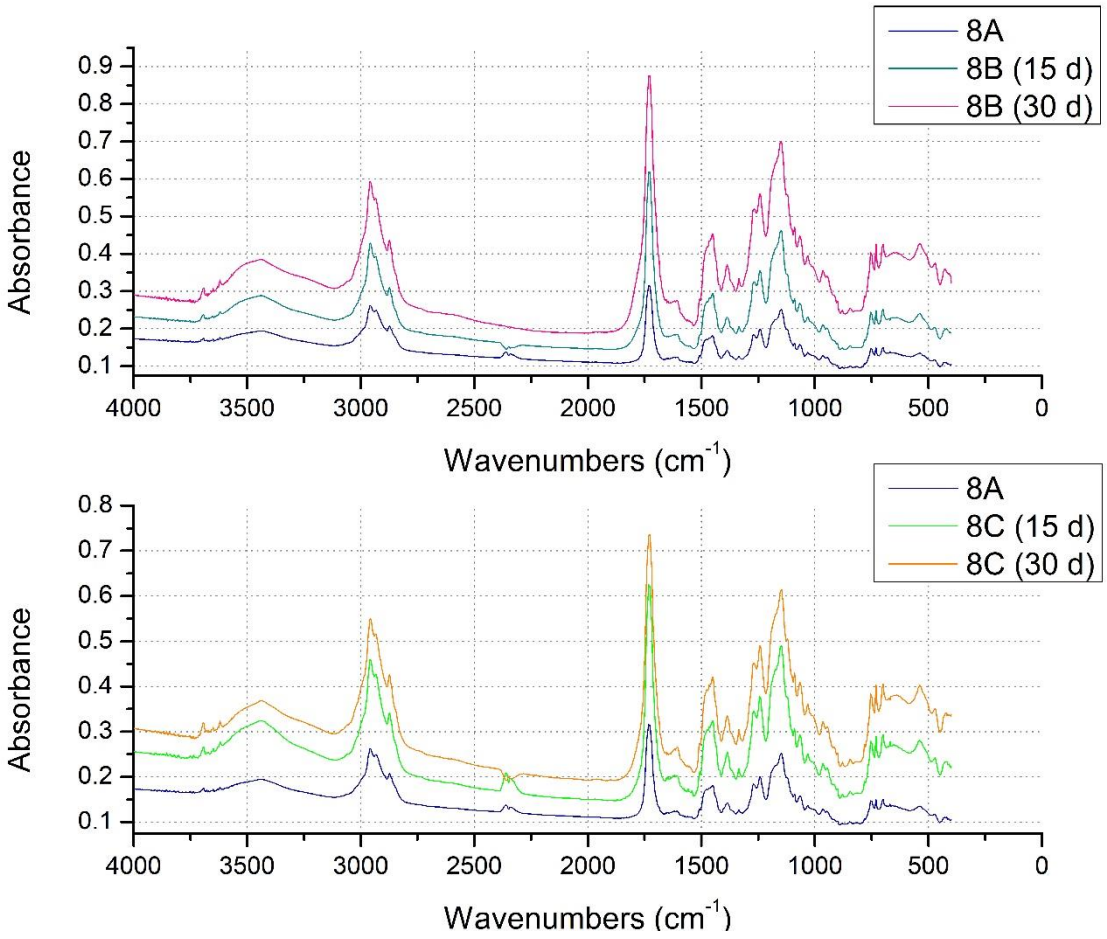


Figure 18 *IR spectra of sample 8.*

- **Green paint**

In sample 9 there were practically no changes in the spectra (Figure 20). And even change in visual appearance (Figure 19) is hard to notice.



Figure 19 *Tiles of sample 9.*

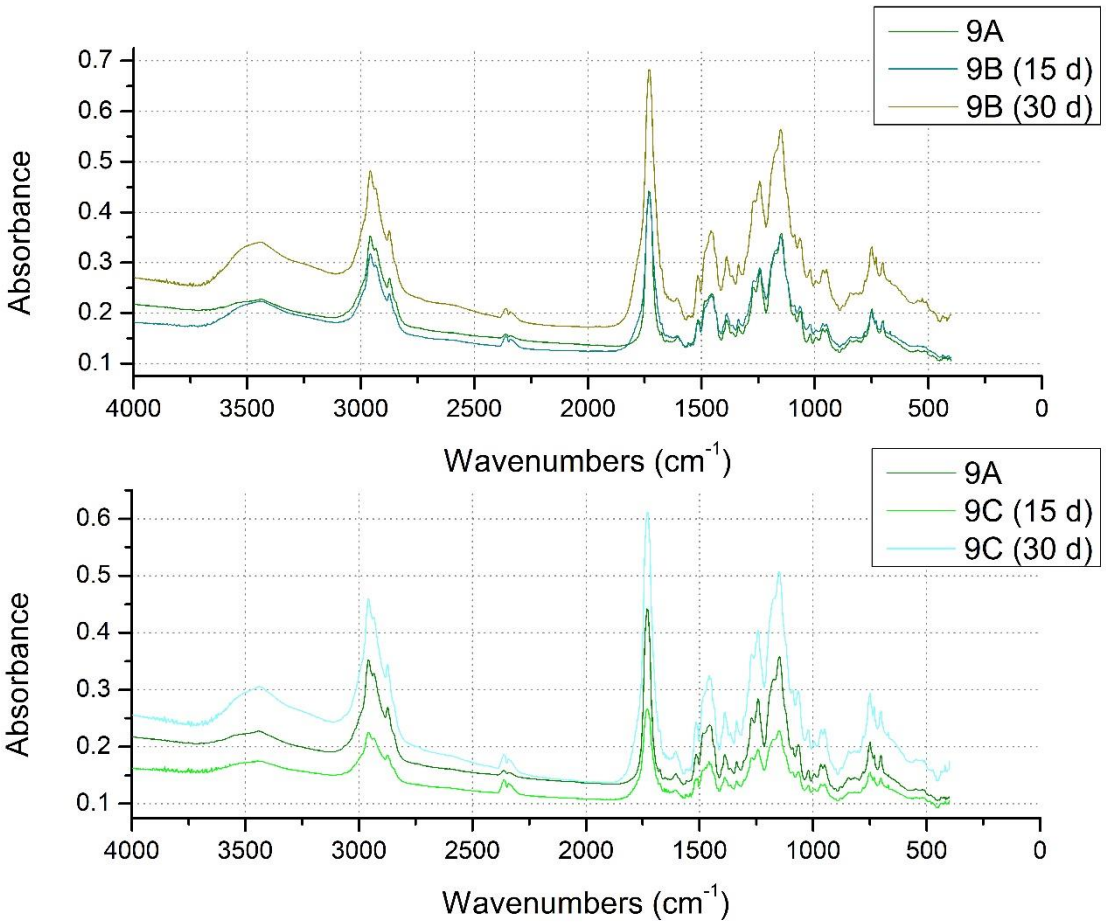


Figure 20 *IR spectra of sample 9 (green).*

4.1.3. German manufacturer (Colors)

We have two brands of the German manufacturer. Here we will represent samples from brand Colors. We have red (sample 12), blue (sample 13), green (sample 14) and yellow (sample 15) paints.

- **Red paint**



Figure 21 *Tiles of sample 12.*

Even though the change of colour on Figure 21 seems obvious, on IR, spectrum peaks for pigments are all preserved.

Results of both experiments are almost the same in this case. This spectra do not have one lone high peak at 1732 cm^{-1} but has one right beside it at 1660 cm^{-1}, which is higher. And here happens the most significant change of spectrum. The peak at 1732 cm^{-1} is slowly getting higher and after 30 days is almost at the height of the peak at 1660 cm^{-1}. On Figure 22 we can see other changes at IR spectrum.

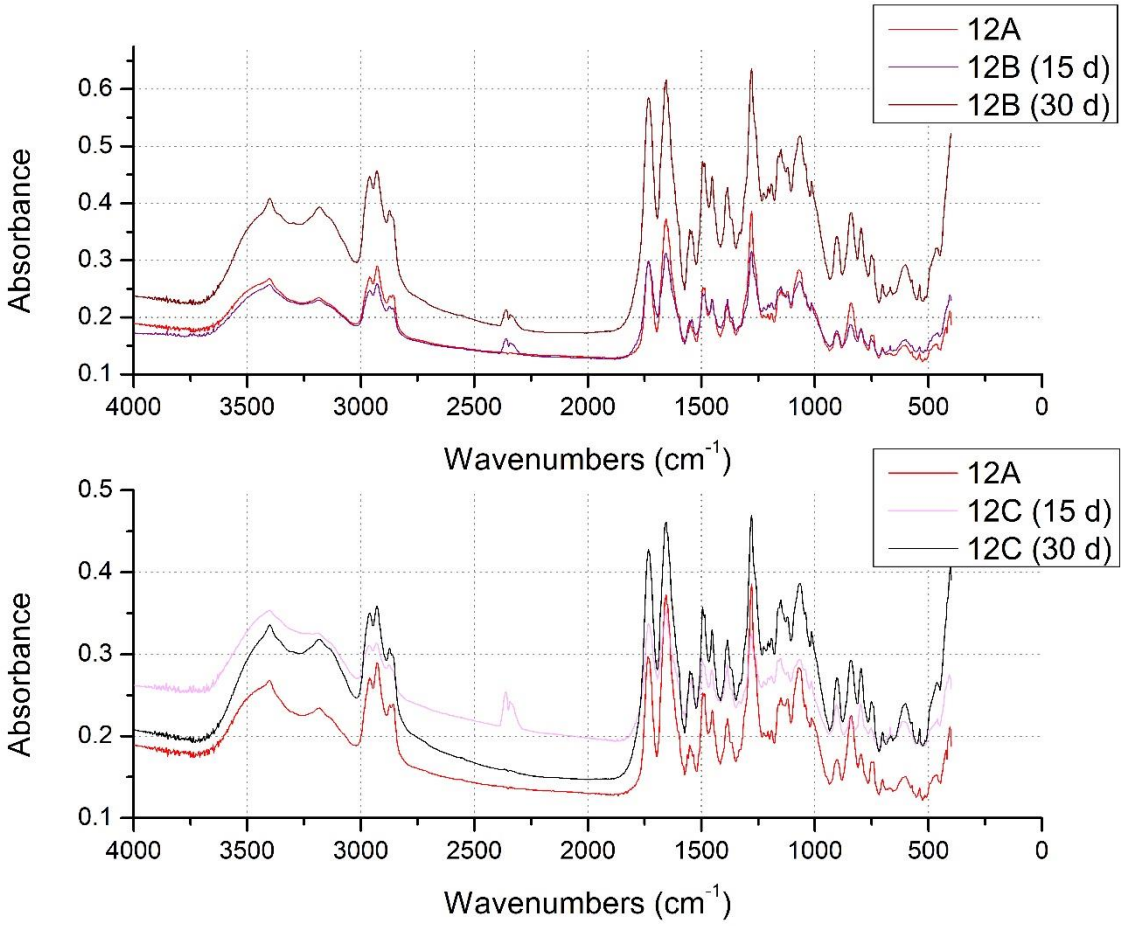


Figure 22 *IR spectra of sample 12.*

- **Blue paint**

This paint also has a distinct double peak (1732 and 1660 cm^{-1}). Like with the sample above, a great change occurs at these two peaks. On Figure 23 we can see that at IR spectrum of the reference sample, peak at 1660 cm^{-1} is higher than the one at 1732 cm^{-1}. In the process of

experiment (series B and C) peak at 1660 cm^{-1} gets lower and peak at 1732 cm^{-1} is getting higher. In series B after 30 days, peak at 1732 cm^{-1} is higher than the other one. In series C peaks are at the same height after 30 days. Also, in series B peak at 2925 cm^{-1} gets higher in the process and is at the end almost equal as signal at 2963 cm^{-1}.

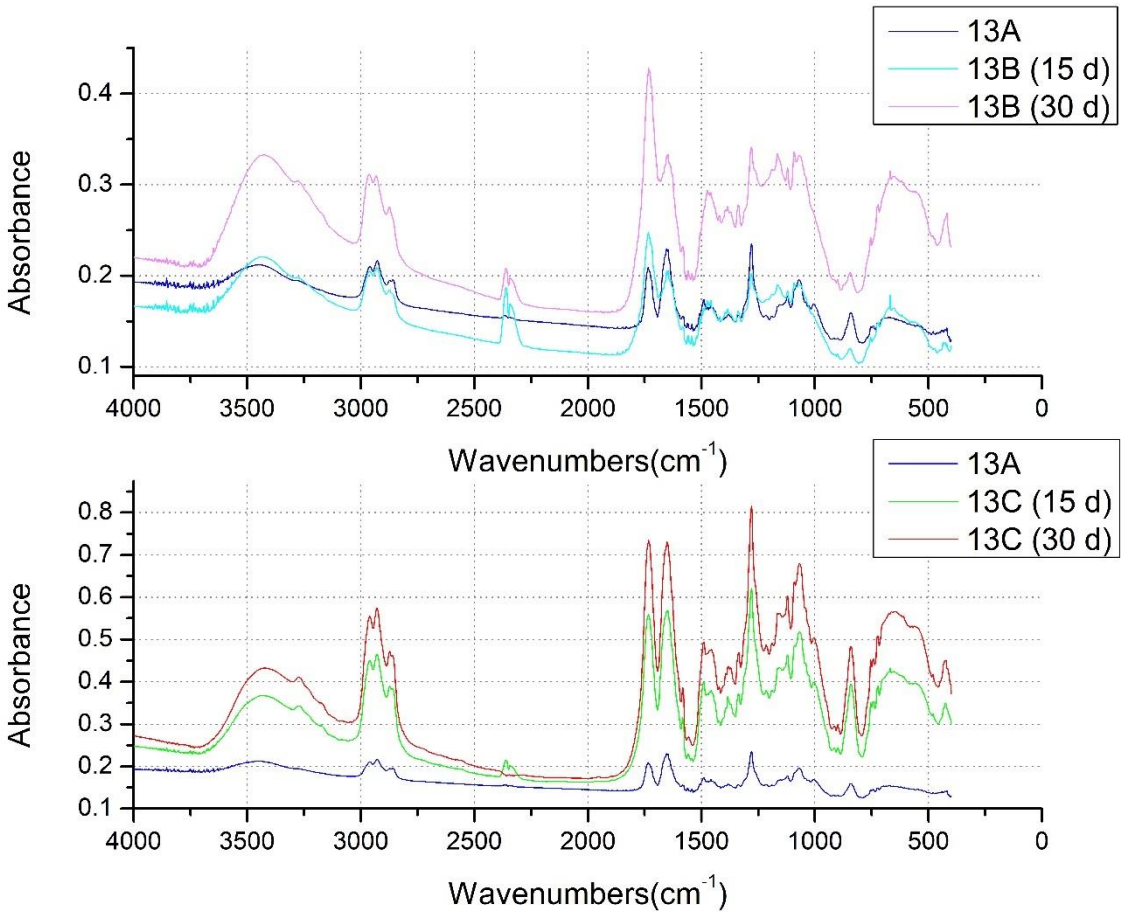


Figure 23 *IR spectra of blue sample 13.*

- **Green paint**

This sample has a triple peak (at 1655, 1690 and 1732 cm^{-1}). In series B some peaks vanish, and some are added, but the main change is happening at those three peaks. At the beginning, the third one (at 1655 cm^{-1}) is the highest, after 15 days it is lower and the other two get higher. At the end of experiment peak at 1690 cm^{-1} is the highest and signal at 1655 cm^{-1} is the lowest of the three.

In series C this change is quicker as we have the same situation as at the end in series B only after 15 days. There are a few new peaks: at 600, 906, 955, 970, 1165 and 1200 cm^{-1} (Figure

24). Another interesting change is the disappearance of peak at the 1280 cm^{-1}. It is a relatively strong peak, but even after only 15 days vanishes.

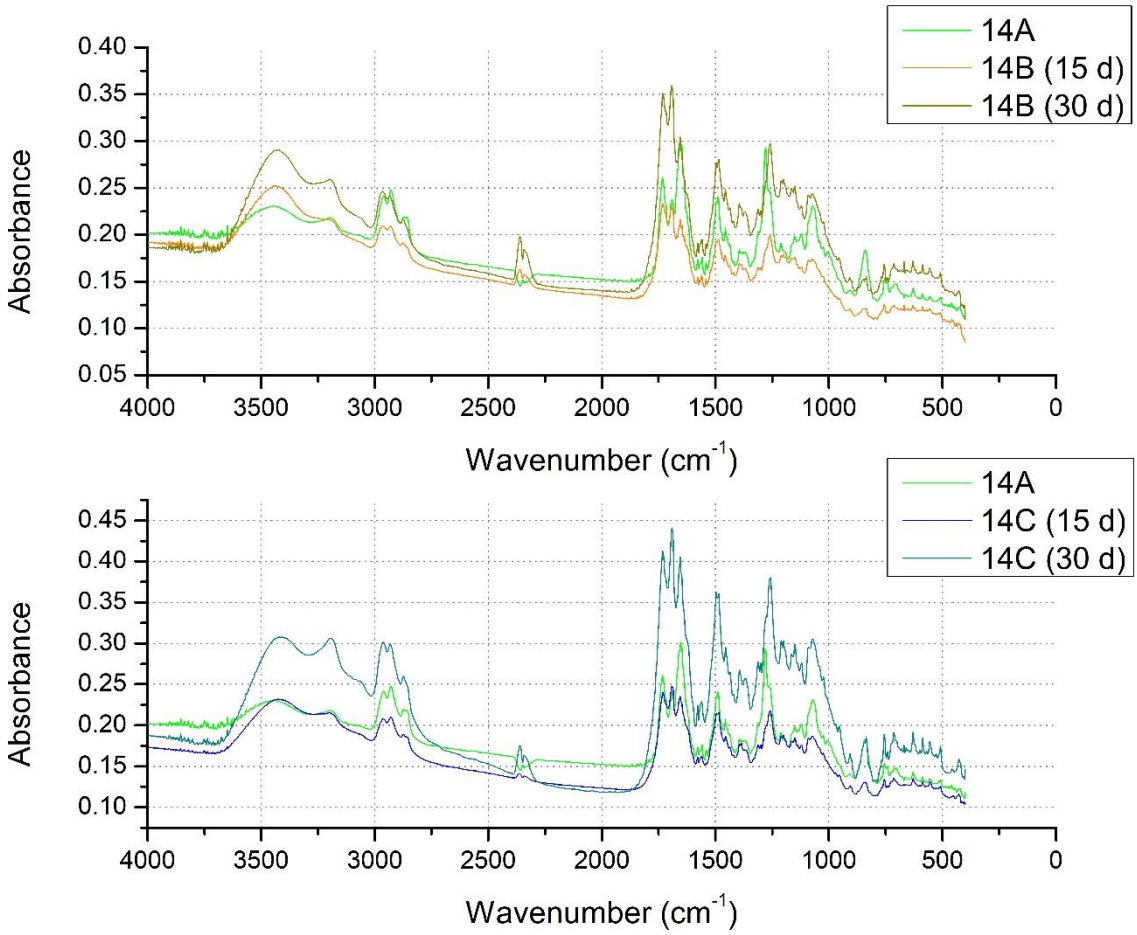


Figure 24 *IR spectra of sample 14*

- **Yellow paint**

As this paint also has the same triple peak as the sample before (sample 14), the changes are the same. The highest peak at the beginning (of those three) is the lowest at the end. Moreover, the lowest becomes the highest.

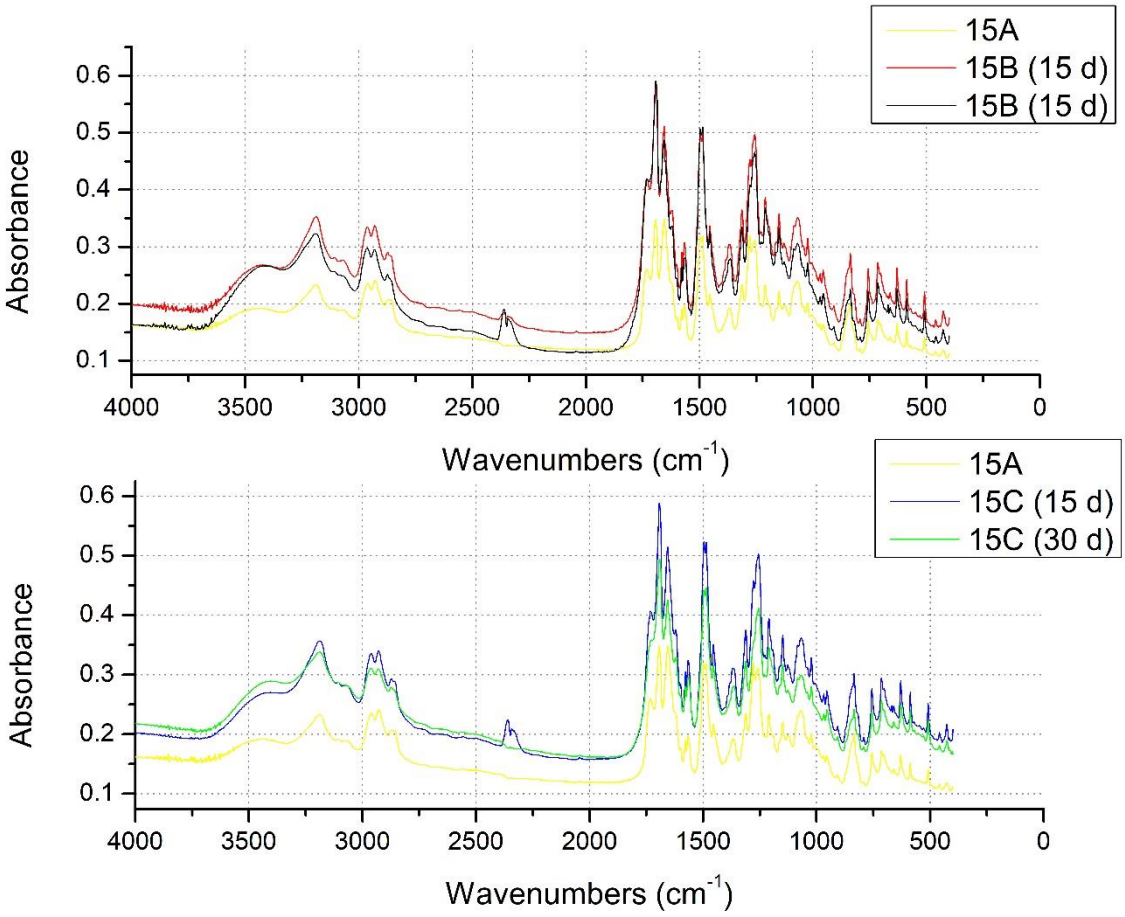


Figure 25 *IR spectra of sample 15*

4.1.4. German manufacturer (Dupli Color)

The last group of sample consist of red (sample 17), blue (sample 18) and green (sample 19) paint.

- **Red paint**

This sample has a two peaks again close together, at 1653 and 1732 cm^{-1}.In series B at first the peak at 1653 cm^{-1} is higher, but at the end of experiment peak at 1732 cm^{-1} is higher. Between those two peaks we obtained a new one at 1685 cm^{-1}. Also peak at 1280 cm^{-1} gets diminished after 15 days and after 30 days completely disappears.

In series C double peak becomes equal at height. All these changes are seen in Figure 26.

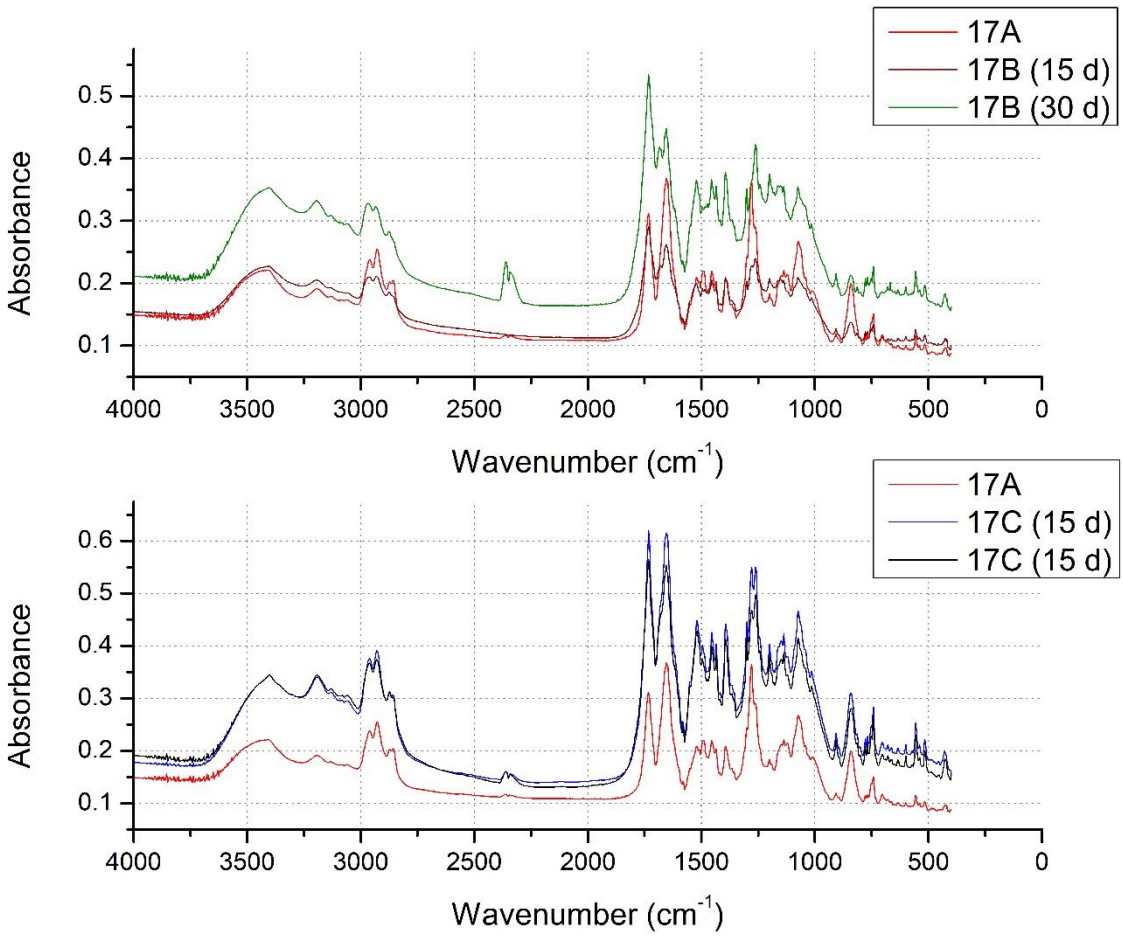


Figure 26 *IR spectra of sample 17*

- **Blue paint**

The only noticeable change in series B and C is at the double peak. At the beginning peak at wavenumber 1635 cm^{-1} is higher. However, through the process, the first peak (at 1732 cm^{-1}) becomes higher. On Figure 27 we see that colour does change even if we cannot define that change at IR spectrum (Figure 28).



Figure 27 *Tiles of sample 18.*

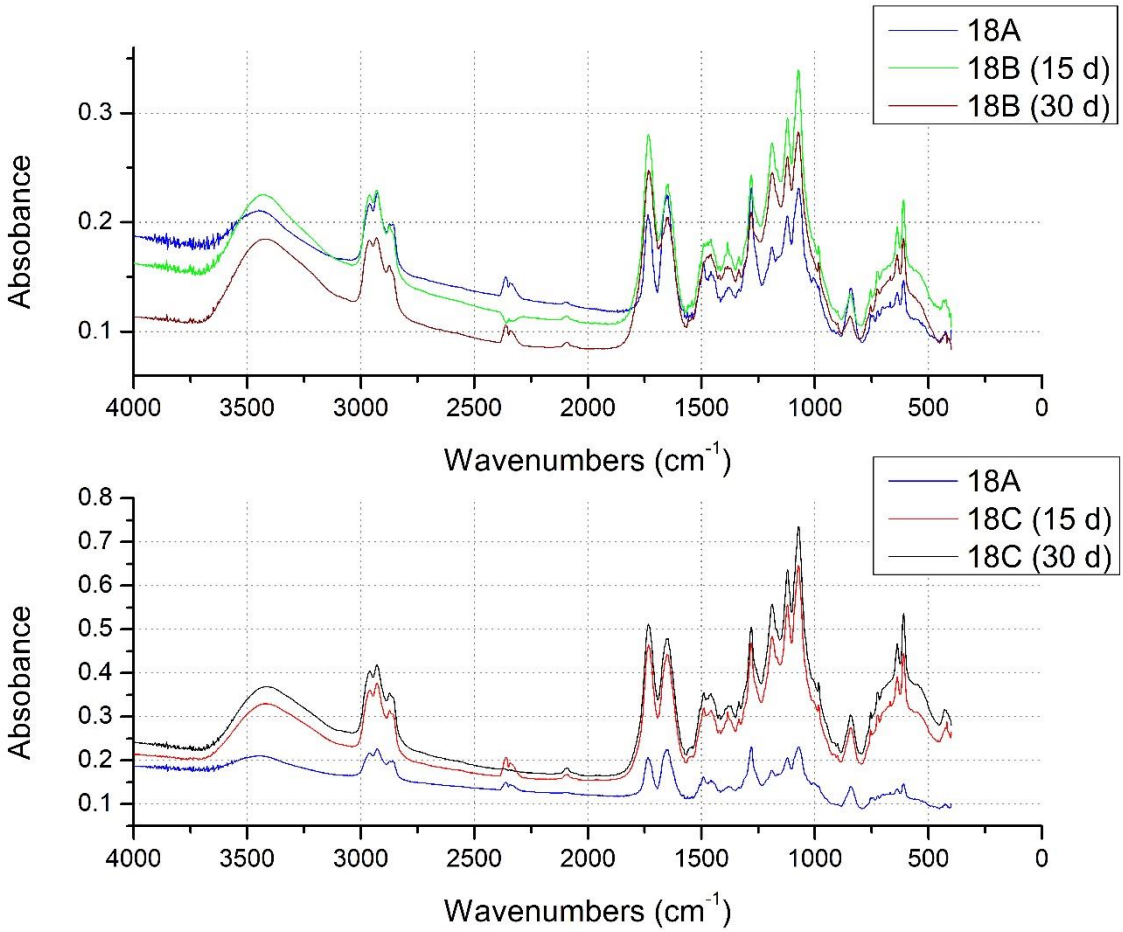


Figure 28 *IR spectra of sample 18.*

- **Green paint**

IR spectrum of this paint also has a double peak (1653 and 1732 cm^{-1}). In both series change around these peaks is the same as in previous samples. The peak at 1653 cm^{-1}, which is higher at first, becomes smaller and at the end the peak at 1732 cm^{-1} is higher. In series B also some peaks vanish, like peaks at 742, 914, 1003, 1027, 1040 and 1070 cm^{-1}. In series C two peaks vanish, one at 1003 and other at 1027 cm^{-1}. Also, in series C we can see two additional peaks (1090 and 1265 cm^{-1}).

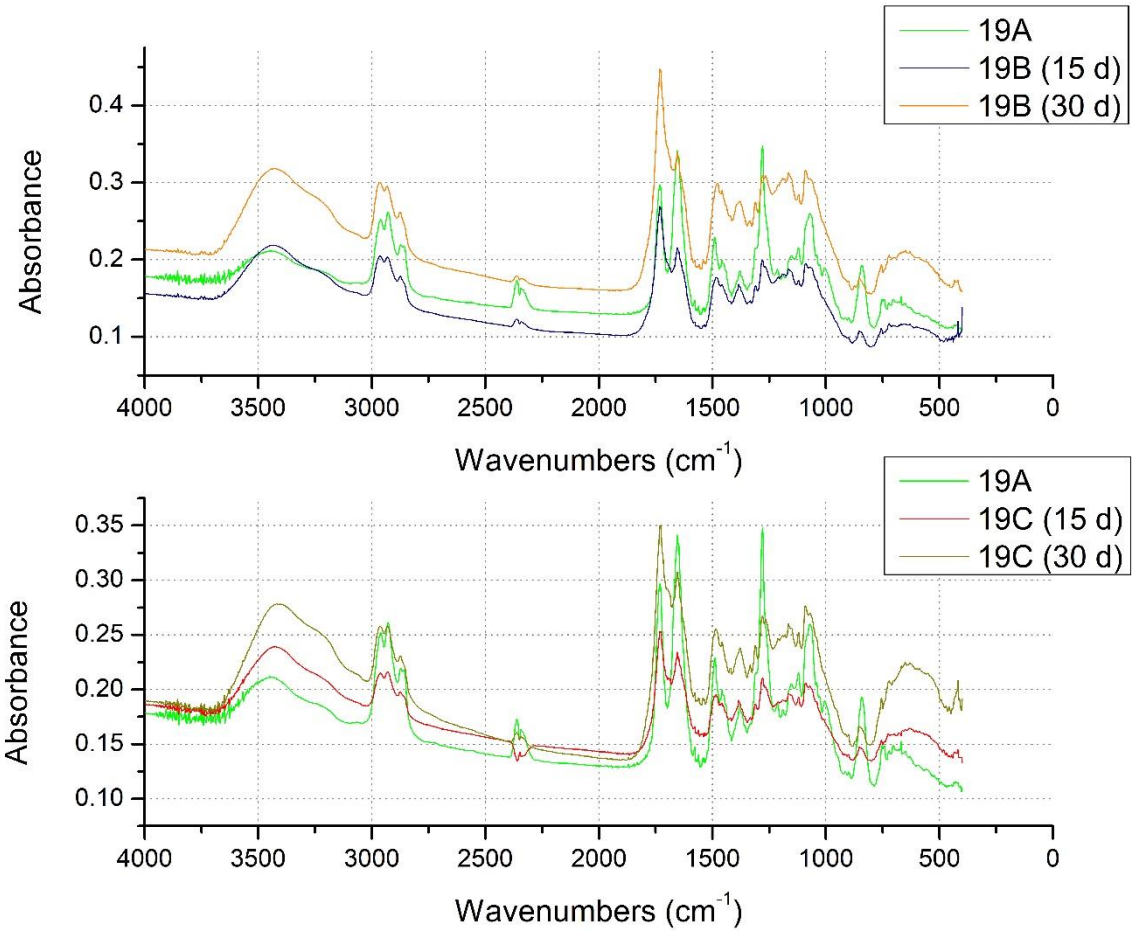


Figure 29 *IR spectra of sample 19*

4.2. MICROSCOPIC ANALYSIS

We took one sample of each colour and looked all three tiles under a microscope. Set A, as mentioned before, is a reference set, set B was for 30 days under UVB light and set C was under UVC light for 30 days. This was not the full microscopic analysis. We only looked how the surface of the paint was affected by UV light.

For yellow we used sample 15. All three images in Figure 30 are taken through the objective with magnification 10x. On image of 15A we can see texture of the dried paint. However, at the image of 15C all texture is gone, and small black spots appeared. Based on this picture, we could conclude that UVC light is more harmful to the topcoat than UVB, but even UVB destroys the texture and the paint becomes "chalky".

Images of red samples were looked at under smaller magnitude, we used objective with magnitude 4x. On Figure 31 we can see that red follows the same tend as yellow. We can see

some kind of a texture at first image (reference sample), less on the second (sample under UVB light for 30 days) and even less on the third (sample under UVC light). Also, on images (Figure 31b) and (Figure 31c) there are spots with, what looks like a nucleus of some kind, in the middle.

Figure 32 shows blue sample under a microscope. This we looked at again with an objective with magnitude 10x. Image (Figure 32a) has a lot of small pores, which could be a consequence of drying method. The second image has some kind of texture, but third image is without any kind of texture.

For green samples we keep the same objective. On Figure 33 we see that green samples only confirmed the trend of other samples. There is a texture in image (Figure 33a), bit less but still present in image (Figure 33b) and nothing useful in image (Figure 33c).

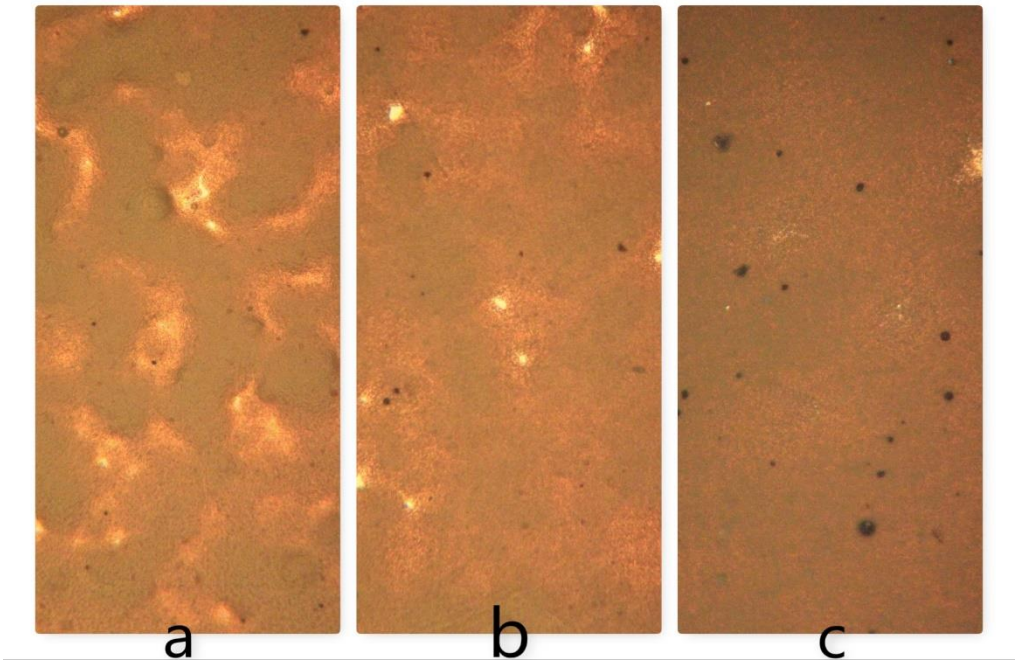


Figure 30 Yellow sample under microscope. (a) 15A, (b)15B, (c)15C.

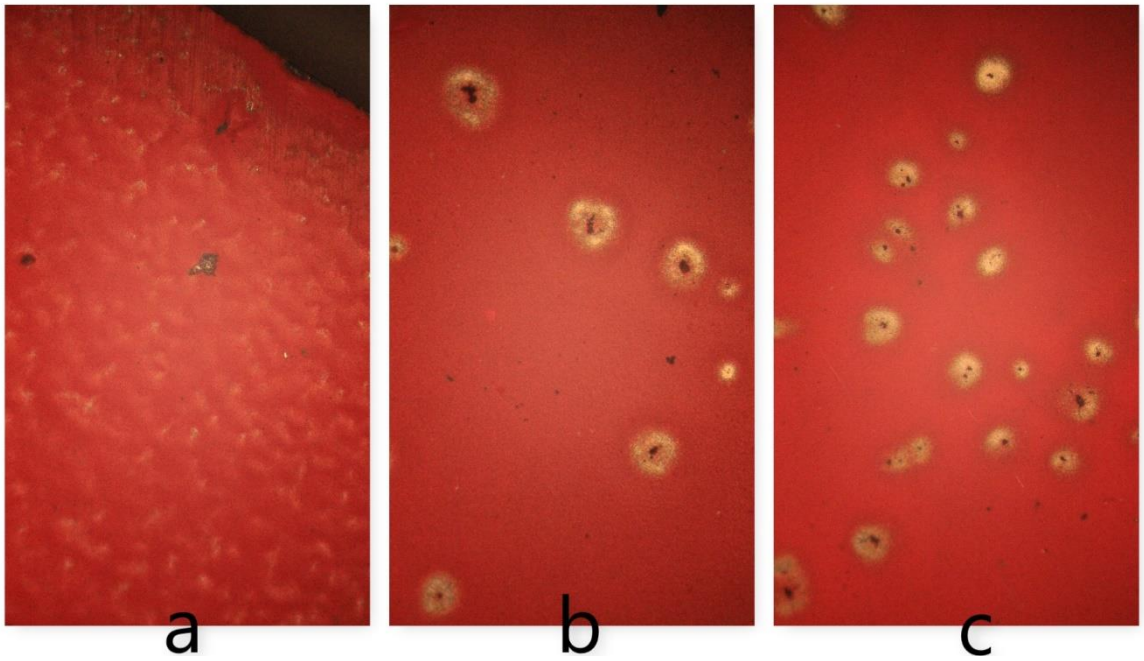


Figure 31 *Red sample under microscope (a) 17A, (b) 17B, (c) 17C.*

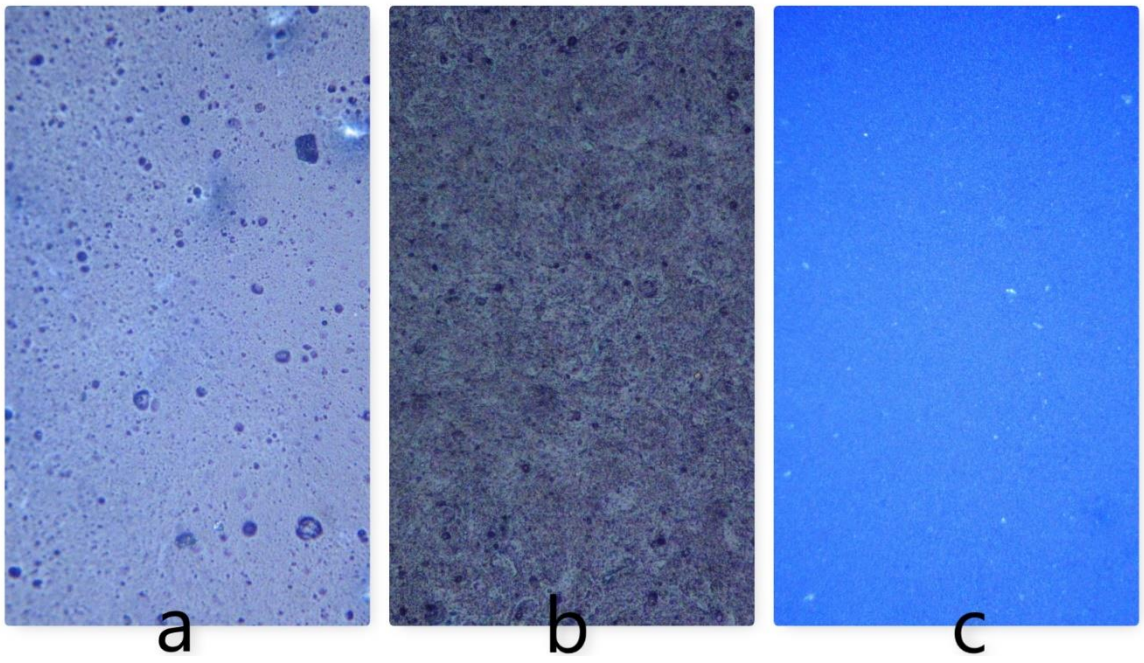


Figure 32 Blue sample under microscope. (a) 8A, (b) 8B, (c) 8C.

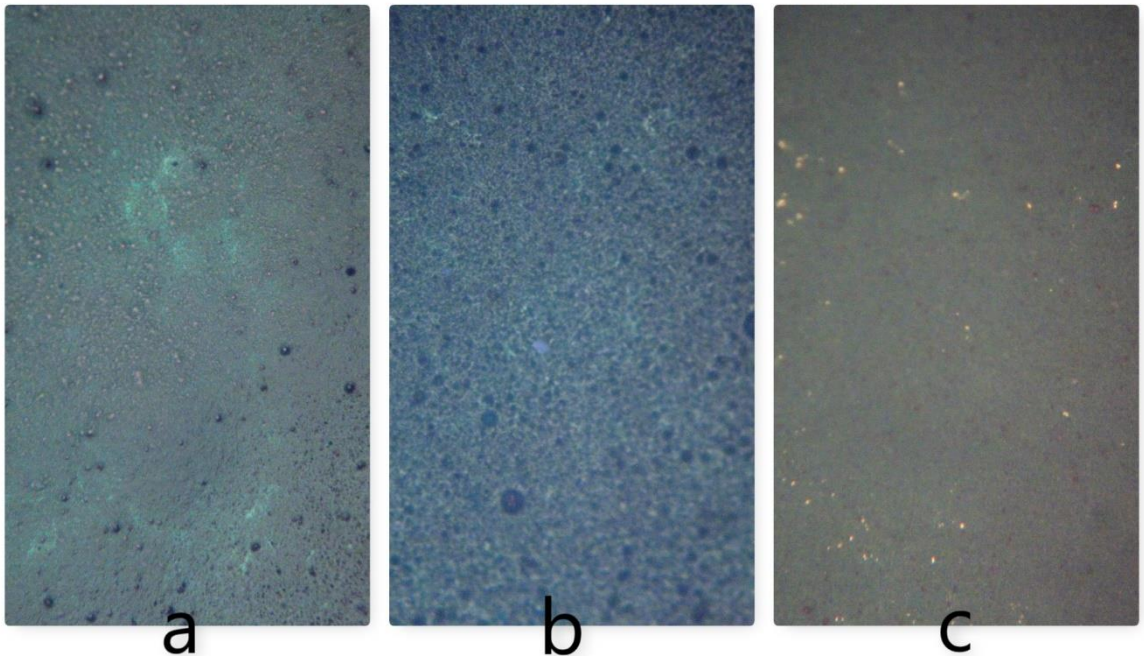


Figure 33 *Green sample under microscope. (a) 4A, (b) 4B, (c) 4C.*

4.3. DISCUSSION [40]

Samples 2, 3, 4, 7, 8 and 9 all have one strong peak at the region reserved for carbonyl groups (C=O, at 1732 cm^{-1}). In the spectra of these samples after 15 and 30 days we see a strengthening of the peaks close to that peak – around 1600 cm^{-1}.

Another group of samples with a similar binder consist of sample 12, 13, 17, 18 and 19. Typical for them are two peaks in close proximity (1732 and 1655 cm^{-1}) and two more groups of peaks (2963, 2925, 2868 and 3400, 3186 cm^{-1}). Exposed to UV light, the first two peaks change intensities. At first the 1655 peak is higher, however through the experiment the peak at 1732 cm^{-1} becomes higher. As we said before, peak at 1732 cm^{-1} represents carboxyl group and peak at 1655 cm^{-1} could be assigned to alkenes. In that case we could assume that double bonds between carbon atoms got broken under UV light, which resulted in lower peak.

We had two samples (14 and 15) who had three peaks in close proximity (1732, 1690 and 1655 cm^{-1}). We already discussed the 1732 and 1655 peaks, but the peak at 1690 cm^{-1} could apply at the presence of aromatic carboxylic acid (especially when we look at the broad peak from 3500 to 3200 cm-1, which represents -OH stretch in carboxylic functional group). As before the peak at 1655 cm^{-1} gets lower and the peak at 1732 cm^{-1} gets higher, but at the end of experiment the highest peak of three is at 1690 cm^{-1}. This could mean that in the process of

decay of this particular binder double bonds between carbon atoms got broken and concentration of aromatic carboxylic acids got higher.

5. CONCLUSIONS

We started this research with 20 samples, but we excluded 7 of them (black and silver colours) because of the hardships of obtaining their IR spectra. The remaining samples were yellow, red, blue and green colour. Samples were left under UVB and UVC light for 30 days. Change of colour was evident to the eye. However, we discovered that in samples, except in case of sample 7, we could not see the change of pigment of a paint exposed to UV light at IR spectra. Also, determination of specific pigment is hard and a bit useless as there are no data of the pigments used in the specific paint spray.

Binders are easier to determine on IR spectra. There are changes at IR spectra that indicate effect of UV light on automotive paints. Combined with other spectroscopic and microscopic methods this can be easily determined. This is important for cases such as sample 17. Under the impact of UV light, sample 17 produced another peak which could imply that another resin is used. Misidentification of the colour used could happen easily, if we would not account for the oldness of the sample. Oldness (in the sense of the amount of time that a sample is exposed to UV light) can be determined by microscopic analysis.

In the regions with a lot of sunlight throughout a year, UV effect of automobile paints is important factor in identification. In the future, a more detailed research of a timeline of UV effect on automobile paints ought to be conducted. Moreover, because of unique climates it would be useful to compose of a database for identification of automobile paints in the region.

6. REFERENCES

1. Zięba-Palus J, Trzcińska B. Application of Infrared and Raman Spectroscopy in Paint Trace Examination. Journal of Forensic Sciences. 2013;58(5):1359-1363.
2. Nieznańska J, Zieba-Palus J, Kościelniak P. Physico-Chemical study of car paints coats. Z Zagadnień Nauk Sadowych. 1999:77-94.
3. Milczarek, Jakub & Zadora, Grzegorz & Zieba-Palus, Janina & Kościelniak, Paweł. Forensic examination of car paints. 2008. Available from: https://www.researchgate.net/publication/294871293_Forensic_examination_of_car_paints
4. 2. The Electromagnetic Spectrum [Internet]. Mini Physics. 2018 [cited 5 September 2018]. Available from: https://www.miniphysics.com/electromagnetic-spectrum_25.html
5. Skoog, Douglas A, F J. Holler, and Stanley R. Crouch. Principles of Instrumental Analysis 7th ed. 2007.
6. Zięba-Palus J, Wąs-Gubała J. An investigation into the use of micro-Raman spectroscopy for the analysis of car paints and single textile fibres. Journal of Molecular Structure. 2011;993(1-3):127-133.
7. Zięba-Palus J, Michalska A, Wesełucha-Birczyńska A. Characterisation of paint samples by infrared and Raman spectroscopy for criminalistic purposes. Journal of Molecular Structure. 2011;993(1-3):134-141.
8. De Gelder J, Vandenabeele P, Govaert F, Moens L. Forensic analysis of automotive paints by Raman spectroscopy. Journal of Raman Spectroscopy. 2005;36(11):1059-1067.
9. Muehlethaler C, Massonnet G, Esseiva P. The application of chemometrics on Infrared and Raman spectra as a tool for the forensic analysis of paints. Forensic Science International. 2011;209(1-3):173-182.
10. Maric M, van Bronswijk W, Lewis S, Pitts K. Synchrotron FTIR characterisation of automotive primer surfacer paint coatings for forensic purposes. Talanta. 2014;118:156-161.

11. Thoonen G, Nys B, Vander Haeghen Y, De Roy G, Scheunders P. Automatic forensic analysis of automotive paints using optical microscopy. Forensic Science International. 2016;259:210-220.
12. Zięba-Palus J, Borusiewicz R. Examination of multilayer paint coats by the use of infrared, Raman and XRF spectroscopy for forensic purposes. Journal of Molecular Structure. 2006;792-793:286-292.
13. Zieba-Palus, J, Trzcińska, BM. Study of pigment composition in paint traces by microspectrometric techniques. Z Zagadnien Nauk Sadowych. 2012;89. 5-16.
14. Chang W, Yu C, Wang C, Tsai Y. A critical evaluation of pectral library searching for the application of automotive paint database. Forensic Science Journal. 2003;2:47-58.
15. Mohseni M, Ramezanzadeh B, Yari H. Effects of environmental conditions on degradation of automotive coatings. New trends and developments in automotive industry. India: Intech Open Access Publisher; 2011. 267–96.
16. Bentley J, Turner GPA. Introduction to Paint Chemistry and principles of paint technology. 4th ed. London: Chapman & Hall. 1998
17. 3. Home Page - Free SDS search [Internet]. Msds.com. 2018 [cited 4 September 2018]. Available from: https://www.msds.com/
18. 4. RAL Colours | RAL Colours history [Internet]. Ral-farben.de. 2018 [cited 31 August 2018]. Available from: https://www.ral-farben.de/content/about-ral-colours/ral-colours-history.html
19. AURASPERSE W-1025 YELLOW OXIDE - FTIR Spectrum - SpectraBase [Internet]. Spectrabase.com. 2018 [cited 2 September 2018]. Available from: https://spectrabase.com/spectrum/DywjJJ1vUxl
20. Iron Oxide Yellow [Internet]. Digitalfire.com. 2018 [cited 2 September 2018]. Available from: https://digitalfire.com/4sight/material/iron_oxide_yellow_876.html
21. PIGMENT YELLOW 12 - FTIR Spectrum - SpectraBase [Internet]. Spectrabase.com. 2018 [cited 2 September 2018]. Available from: https://spectrabase.com/spectrum/A2ilrK93OnM
22. Pigment Yellow 12 [Internet]. En.wikipedia.org. 2018 [cited 2 September 2018]. Available from: https://en.wikipedia.org/wiki/Pigment_Yellow_12

23. PIGMENT RED 5 - FTIR Spectrum - SpectraBase [Internet]. Spectrabase.com. 2018 [cited 3 September 2018]. Available from: https://spectrabase.com/spectrum/KZ7WKQKJ2MC
24. C.I. Pigment Red 5 [Internet]. Pubchem.ncbi.nlm.nih.gov. 2018 [cited 3 September 2018]. Available from: https://pubchem.ncbi.nlm.nih.gov/compound/73555232#section=Names-and-Identifiers
25. PIGMENT RED 220 - FTIR Spectrum - SpectraBase [Internet]. Spectrabase.com. 2018 [cited 3 September 2018]. Available from: https://spectrabase.com/spectrum/CzVRYjEHzrq
26. PIGMENT RED 48 - FTIR Spectrum - SpectraBase [Internet]. Spectrabase.com. 2018 [cited 3 September 2018]. Available from: https://spectrabase.com/spectrum/4lg8RDVudQZ
27. PIGMENT BLUE 60 - FTIR Spectrum - SpectraBase [Internet]. Spectrabase.com. 2018 [cited 3 September 2018]. Available from: https://spectrabase.com/spectrum/IqLVDwm7mmf
28. Indanthrene blue | C28H14N2O4 | ChemSpider [Internet]. Chemspider.com. 2018 [cited 3 September 2018]. Available from: http://www.chemspider.com/Chemical-Structure.6435.html?rid=1505f32b-3dd5-406c-95d0-a5e7d9c7c256
29. COBALT BLUE 767 - FTIR Spectrum - SpectraBase [Internet]. Spectrabase.com. 2018 [cited 3 September 2018]. Available from: https://spectrabase.com/spectrum/Lf65Lkr0cyj
30. Aluminum cobalt oxide [Internet]. Pubchem.ncbi.nlm.nih.gov. 2018 [cited 3 September 2018]. Available from: https://pubchem.ncbi.nlm.nih.gov/compound/159384#section=Related-Records
31. PIGMENT GREEN 7 - FTIR Spectrum - SpectraBase [Internet]. Spectrabase.com. 2018 [cited 3 September 2018]. Available from: https://spectrabase.com/spectrum/8jHYeJlzbNQ
32. Phthalo green | C32Cl16CuN8 | ChemSpider [Internet]. Chemspider.com. 2018 [cited 3 September 2018]. Available from: http://www.chemspider.com/Chemical-Structure.21781844.html?rid=c1764ed0-2411-46fa-9406-b64b0efcac16&page_num=0

33. PIGMENT GREEN 10 - FTIR Spectrum - SpectraBase [Internet]. Spectrabase.com. 2018 [cited 3 September 2018]. Available from: https://spectrabase.com/spectrum/EIOsdoFftfb
34. CHROMIUM(III) OXIDE - FTIR Spectrum - SpectraBase [Internet]. Spectrabase.com. 2018 [cited 3 September 2018]. Available from: https://spectrabase.com/spectrum/528bMulPI66
35. Chromium(III) oxide | Cr2O3 | ChemSpider [Internet]. Chemspider.com. 2018 [cited 3 September 2018]. Available from: http://www.chemspider.com/Chemical-Structure.451305.html?rid=60d46172-96ad-40ee-8f8c-730835411967
36. PIGMENT GREEN 36 - FTIR Spectrum - SpectraBase [Internet]. Spectrabase.com. 2018 [cited 3 September 2018]. Available from: https://spectrabase.com/spectrum/9VQP5Yy3IRD
37. [Internet]. Photos.labwrench.com. 2018 [cited 4 September 2018]. Available from: http://photos.labwrench.com/equipmentManuals/7783-2914.pdf
38. Fourier Transform and Apodization : SHIMADZU (Shimadzu Corporation) [Internet]. Shimadzu.com. 2018 [cited 4 September 2018]. Available from: https://www.shimadzu.com/an/ftir/support/tips/letter15/apodization.html
39. Polarized Light Microscopy [Internet]. Nikon's MicroscopyU. 2018 [cited 4 September 2018]. Available from: https://www.microscopyu.com/techniques/polarized-light/polarized-light-microscopy
40. Humecki H. Practical guide to infrared microspectroscopy. New York, N.Y.: Dekker; 1995.

7. Abstract

Testing of the UV light effect on the automotive paints by FTIR spectroscopy

Identification of paint traces by FTIR spectroscopy is a recognized forensic method. It is especially important in a hit and run car accidents.

The objective was to discover how automotive paints exposed to UV light are affected.

Methods we used were FTIR spectroscopy and polarised microscopy.

Our primary results were IR spectra of 13 samples. We used samples from a few manufacturers in yellow, red, blue and green colour. Spray paints were applied on stainless steel and left under UVB (UV light with a wavelength of 304 nm) and UVC (UV light with a wavelength of 254 nm) for 30 days. We obtained IR spectra of samples after 15 and 30 days.

We concluded that samples visibly changed after the experiment. We saw some interesting modifications of IR spectra, which could give us an information of what is happening in car paint sample when exposed to UV light.

Keywords: automotive paints, IR spectroscopy, UVC, UVB

Sažetak

Ispitivanje učinka UV svjetla na automobilske boje pomoću FTIR spektroskopije

Identifikacija tragova boja s pomoću FTIR spektroskopije je poznata forenzična metoda koja se koristi pri ispitivanjima automobilskih nesreća.

Cilj je bio saznati kako se mijenjaju automobilske boje izložene UV svjetlu.

Metode koje smo koristili bile su FTIR spektroskopija i analiza s polarizirajućim mikroskopom.

Naši primarni rezultati bili su IR spektri 13 uzoraka. Koristili smo uzorke nekoliko proizvođača u žutoj, crvenoj, plavoj i zelenoj boji. Boje za raspršivanje nanesene su na pločice od nehrđajućeg čelika i ostavljene pod UVB (UV svjetlo s valnom duljinom od 304 nm) i UVC (UV svjetlo s valnom duljinom od 254 nm) tijekom 30 dana. Nakon 15 i 30 dana dobili smo IR spektre uzoraka.

Ustanovili smo da su se uzorci vidno izmijenjili nakon eksperimenta. U IR spektrima smo primjetili promjene inteziteta te pojavu i nestanak pojedinih vrpci kod boja koje su bile izložene UV svijetlu u odnosu na referentne uzorke. Ti podaci bi nam mogli dati informacije o tome što se događa u uzorku automobilske boje kada je izložena UV svjetlu.

Ključne rječi: automobilske boje, IR spektroskopija, UVC, UVB

CURRICULUM VITAE

Terezija Vodišek
Stopce 3
3270 Laško
Slovenija
trezivodisek@gmail.com

Date of Birth: 28.09.1992
Place of Birth: Celje
Country of Birth: Slovenia

Education:

2016-2018	Forensic chemistry and molecular biology, University department for forensic sciences, University of Split
2011-2015	Chemical Technology, Faculty of Chemistry and Chemical Engineering, University of Maribor
2007-2011	Gimnazija Lava Celje, High School
1999-2007	Osnovna Šola Primoža Trubarja Laško, Primary School

(APPENDIX 3)

UNIVERSITY OF SPLIT

University Department of Forensic Sciences

Statement on academic integrity

I, **Terezija Vodišek**, hereby declare and confirm with my signature that my master's thesis with title: **Testing of the UV light effect on the automotive paints by FTIR spectroscopy**

is result of my own autonomous work based on my research and literature published, which is seen in the notes and bibliography used.

I also declare that no part of the paper submitted has been made in an inappropriate way, whether by plagiarizing or infringing on any third person's copyright.

Finally, I declare that no part of the paper submitted has been used for any other paper in another higher education institution, research institution or educational institution.

The content of my paper fully corresponds to the content of defended and after the defence edited paper.

Split, _____

Student signature: _____