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## The influence of the type of thermal stabilizer on the graying of poly(vinyl chloride) compositions under the action of UV light and moisture

**Abstract:** In some cases, in the initial stages of exposure to atmospheric conditions, gray discoloration appears on the surface of PVC products pigmented with titanium white. The aim of the study was to develop a simple method for determining the likelihood of discoloration of a PVC/thermal stabilizer/titanium white composition at the onset of exposure to UV radiation. Common thermal stabilizers were used to determine which of them, combined with a polymer and  $\text{TiO}_2$ , can cause discoloration of the samples when exposed to UV radiation, especially in the presence of water. It has been shown that discoloration of a PVC composition surface exposed to UV radiation occurs only in the case of lead stabilizers. Discoloration did not occur when tin stabilizers and Ca/Zn were used in the PVC compositions. Only areas exposed to  $\text{H}_2\text{O}$  during exposure to UV radiation were affected.

**Keywords:** Poly(vinyl chloride), Titanium dioxide, Lead stabilizer, Graying, Weathering, UV exposure

### WPLYW RODZAJU STABILIZATORA TERMICZNEGO NA SZARZENIE KOMPOZYCJI POLI(CHLORKU WINYLU) POD WPLYWEM DZIAŁANIA PROMIENIOWANIA UV I WILGOCI

**Streszczenie:** W niektórych przypadkach na powierzchni wyrobów z PVC pigmentowanych białą tytanową w początkowym etapie ekspozycji w warunkach atmosferycznych, pojawiają się szare przebarwienia. Niniejsza praca miała na celu opracowanie prostej metody określenia prawdopodobieństwa wystąpienia szarzenia kompozycji PVC/stabilizator termiczny/biel tytanowa w początkowym etapie ekspozycji na działanie promieniowania UV. Wykazano, że szarzenie powierzchniowe kompozycji PVC pod wpływem działania promieniowania UV, występuje jedynie w przypadku zastosowania stabilizatorów ołowiwych. Zjawiska tego nie stwierdzono w przypadku stosowania w kompozycjach PVC stabilizatorów cynowych jak również Ca/Zn. Szarzeniu ulegają jedynie miejsca mające kontakt z  $\text{H}_2\text{O}$  podczas napromienienia UV.

**Słowa kluczowe:** poli(chlorek winylu), ditlenek tytanu, stabilizatory ołowiove, szarzenie, starzenie naturalne, promieniowanie UV.

### INTRODUCTION

Thermal stabilizers need to be included in compositions of poly(vinyl chloride) in the course of processing to protect them against thermal (heat) and mechanical (shear stress) degradation. Thermal stabilizers, used in the

processing of poly (vinyl chloride), serve mainly to:

- eliminate the catalytic action of various factors actively contributing to the thermal degradation of the polymer;
- reduce the speed of PVC dehydrochlorination by increasing its stability by means of

chemical interaction with the added stabilizers;

— prevent cross-linking of macro-molecules.

One of the basic ways of stabilizing PVC, making it possible to reduce the amount of potential locations where polymer dechlorination may begin, is introducing labile chlorine atoms. Salts of Pb, Zn, Ca, Sr, Mg, Na, Li, Ba, Cd of the following acids: sulphuric, carbonic, phosphoric, stearic, palmitic, lauric, phthalic, fumaric, maleic, salicylic, benzoic and their mixtures, have a stabilizing effect on PVC.

Organic stabilizers complement this group of stabilizers. They include – organotin compounds, organic phosphites, epoxy compounds, aminocrotonates and  $\alpha$ -phenylindoles.

Currently, the following stabilizers are commonly used in the production of extruded elements made of poly (vinyl chloride): lead, organotin, Ca/Zn and organic stabilizers.

In the process of weathering of PVC under natural atmospheric conditions, degradation of the polymer occurs by separation of labile chlorine atoms, leading to the formation of polyene sequences, which, in contact with the surrounding oxygen, form  $\alpha, \alpha'$ -dichloroloketones, aryl chlorides,  $\gamma$ -laktones and esters of percarboxylic acids (during photo-oxidation reactions) [1,2,3].

PVC compositions dyed white, which are intended for the manufacture of products used outdoors, most commonly contain a rutile variety of titanium dioxide.

Titanium dioxide is found in three polymorphic varieties: tetragonal anatase and rutile, and rhombic brookite [4, 5, 6]. The most thermodynamically durable polymorphic variation of  $\text{TiO}_2$  is rutile, while anatase is a meta-stable species. The process of transition from anatase to rutile is an irreversible reaction and takes place at a temperature of 400-800°C.

Titanium dioxide belongs to the group of redundant semiconductors (type n). Various energy values of the band gap are associated with the position of the lower edge of the conduction band, which for each polymorphic variety is located at another level [7,8]. Titanium

dioxide is a semiconductor which is sensitive to radiation and which absorbs electromagnetic radiation near the UV range. The energy difference between the valence and conductivity bands in solid state is 3.05 eV for rutile and 3.29 for anatase, for an absorption band of <415nm for rutile and <385nm for anatase correspondingly [9]. The absorption of radiation energy leads to the excitation of a valence band electron and its dislocation into the conductivity band. The electron and the electron hole are mobile. They can move around on the surface of a solid and are involved in redox reactions.

Titanium dioxide is amphoteric, its surface is saturated by coordinatively bound water, which subsequently creates hydroxyl ions. Depending on the type of binding of the hydroxyl groups with titanium, they can either be acidic or alkaline in nature. The surface of  $\text{TiO}_2$  is thus polar at all times. Coverage of the surface with hydroxyl groups has a decisive influence on the properties of the pigment as well as its dispersion and resistance to weather conditions. The presence of hydroxyl groups enables the induction of photochemical reactions e.g. decomposition of water or a reduction of nitrogen to ammonia.

Typically, the surface of the  $\text{TiO}_2$  used in the processing of PVC is modified with various inorganic/organic compounds, for example with aluminum oxides, silicon or zirconium, affecting the optical activity of the pigment.

Rutile and anatase varieties show intensive photocatalytic activity, which is utilized in the photocatalytic degradation of contamination both in solutions and in the gas phase.

On the basis of a measurement of the efficiency of the decomposition of salicylic acid and phenol, the photoactivity of  $\text{TiO}_2$  coated with silica and aluminum oxide was evaluated [10]. It was shown that silica-coated  $\text{TiO}_2$  consists of a deposit of isolated particles, which was not found in  $\text{TiO}_2$  coated with aluminum oxide. This is most probably why the effectiveness of photoreaction inhibition in the case of silica is higher and it is estimated at 20%, while for aluminum it is only 5%.

The catalytic activity of titanium dioxide pigment, which is used in polymer materials, is not desired.

Much work has been devoted to studying the impact of TiO<sub>2</sub> on the degradation of PVC [1,2,11-17], but its role has not been ultimately explained yet, especially given the presence of other additives in the polymer composition. In some studies [14-15] it is claimed that protection against PVC degradation mainly involves the physical absorption of UV by TiO<sub>2</sub>, particularly in the case of coated pigment grains. It was proven that TiO<sub>2</sub> can be activated by UV, water and oxygen, accelerating thus the degradation of the polymer [11, 12, 15].

Thermal stabilizers do not participate in oxidation processes which are preceded by elimination reactions in the course of PVC degradation. In turn, TiO<sub>2</sub> pigments prevent processes of elimination through the absorption of UV radiation. However, they catalyze oxidation reactions [16]. However, it is not clear whether they directly oxidize PVC macromolecules or the polyene sequences in a polymer.

Elimination reactions are caused by the action of heat and UV radiation and lead to changes in transparency, clarity and color of PVC products. Oxidation reactions take place in the thin 200 μm surface layers due to the limited diffusion of oxygen into the polymer matrix. However, they cause surface cracking and increased surface roughness [16]. In practice, this results in the chalking of the surface.

The successive cycles of chalking of titanium dioxide caused by the absorption of UV radiation were suggested by Winkler [18].

UV absorption by TiO<sub>2</sub> leads to a transfer of electrons from the valence band to the conduction band, leaving positively charged „holes“ in the valence band. In this way, the subsequent steps in the reaction, i.e. the so-called chalking cycle, are initiated, eventually resulting to the formation of hydroxyl and hydroperoxide radicals.

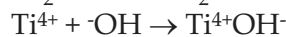
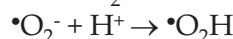
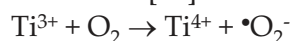
According to Gesenhues and Lemaire, only oxidation reactions are catalyzed by TiO<sub>2</sub> [2,11,19]. Its mechanism of action may be pre-

sented as follows. In the presence of water, hydroxyl Ti<sup>4+</sup>OH<sup>-</sup> groups are formed on the surface of TiO<sub>2</sub>.

The irradiation energy of TiO<sub>2</sub>, which exceeds the band-gap energy (3.05 eV) leads to the formation of surface hydroxyl radicals, which can be converted to hydroperoxides, which promote radical polymer degradation reactions.

In these processes, Ti<sup>4+</sup> (IV) ions become reduced to Ti<sup>3+</sup> (III), which often produces a gray discoloration of a PVC sample [14, 15, 20].

In turn, Ti<sup>3+</sup> ions (III) oxidize to Ti<sup>4+</sup> (IV), leading, in the presence of oxygen, to the formation of hydroperoxide radicals on the surface of TiO<sub>2</sub> by interacting with the damp surface or water [21].



The reaction of these radicals with macromolecules normally leads to a photocatalytic degradation of the polymer.

In an aqueous environment, a TiO<sub>2</sub> – H<sub>2</sub>O interphase double-layer surface forms, which gives the particles the qualities of a capacitor. These processes can have a significant impact on the nature of all interphase charge transfers into the surrounding polymer matrix, and thus on the likelihood of discoloration.

It was found that both in coating systems as well as PVC products, water is a key factor determining the catalytic activity of TiO<sub>2</sub>, and therefore the rehydroxylation of the TiO<sub>2</sub> surface must be a factor determining the rate of the steps in the photocatalytic cycle [17,22]. There are currently no published studies relating to the impact of rainwater on the photocatalytic activity of TiO<sub>2</sub> in materials made of PVC.

Apparent grey discoloration on lead-bearing TiO<sub>2</sub> coated PVC products may appear as early as in the initial stages of exposure in atmospheric conditions.

It is thought that this color change is caused by photochemical reactions between the lead stabilizer and TiO<sub>2</sub>. Under the influence of UV radiation, Ti<sup>4+</sup> is reduced to Ti<sup>3+</sup>. Afterwards,

Ti<sup>3+</sup> reduces Pb<sup>2+</sup> down to metallic Pb<sup>0</sup>, which causes the graying of the exposed surface. In turn, atmospheric oxygen can cause oxidation of Pb<sup>0</sup> to Pb<sup>2+</sup> as a result of which the color returns to its initial state [23, 24].

Gesenhues believes that graying is the result of the surface reduction of TiO<sub>2</sub>. Its color returns to normal, when the pigment is exposed to the air in the later stages of PVC degradation [17].

However, these studies do not explain why the surface reduction takes place only in the case of lead stabilization of PVC products, and does not occur when Ca/Zn or tin stabilizers are used. Besides, graying is also dependent on the type of TiO<sub>2</sub> used.

In addition to graying, which takes place in the early stages of changes on the surface of products made of unplasticized PVC (stabilized with lead compounds) exposed to solar radiation, other types of discoloration appearing on their surface, are also relevant [25]. The phenomenon of „pinking” of PVC sections during outdoor exposure has been thoroughly discussed by Edge et al. [21].

Below are some factors which cause discoloration of PVC sections during their use in outdoor conditions: type of titanium dioxide used in the manufacture of sections, type of thermal stabilization used as well as the type and quantity of antioxidants in the PVC composition.

The aim of the study was to develop a simple method for determining the likelihood of discoloration of a PVC /thermal stabilizer/titanium white composition at the onset of exposure to UV radiation. The most common thermal stabilizers were used to determine which

of them, combined with a polymer and TiO<sub>2</sub>, can cause discoloration of the samples when exposed to UV radiation, especially in the presence of water.

## EXPERIMENTAL

Simulations were made of the impact of UV radiation and distilled water/aqueous solution of hydrochloric acid (1:1) on the discoloration of the film surface of a PVC/stabilizer/titanium white composition. Color changes taking place on the surface of film as a result of the action of UV radiation and distilled water/aqueous solution of hydrochloric acid (1:1) were examined. For this purpose, a designated area of the sample in the form of film was wetted by applying drops of distilled water/hydrochloric acid solution (1:1) and was exposed to UV radiation for 5, 10, 20 and 30 minutes using a UV lamp Type Emita VP-60 (FAMED, Poland), 180W, 220 V, 50 Hz. Samples were placed at a constant distance (10 cm) from the lamp at a dose rate of 23,7 KJ/m<sup>2</sup>. Color changes occurring on the surface of the samples were observed in the places where the drops were applied.

Afterwards, drops of an aqueous solution of H<sub>2</sub>S were applied on the samples exposed to UV radiation in areas wetted with water/HCl solution.

## Materials

PVC compositions were prepared using the following materials:

– thermal stabilizers-list in Table 1,

**Tab. 1. Stabilizers used in PVC mixtures**

Name	Type of stabilizer	Producer
Stabilox CZ 2028GN	calcium-zinc (1)	Reagens GmbH
Baeropan MC 90705 FP	calcium-zinc (2)	Baerlocher GmbH
Baerostab Pebefos FP (dibasic lead phosphite)	lead (inorganic)	Baerlocher GmbH
Assua 55A (tribasic lead sulfate/ dibasic lead stearate)	lead (inorganic-organic)	Cortex Chemicals
Baerostab Pb 28 f (neutral lead stearate)	lead (organic)	Baerlocher GmbH
Ergoterm OTGO-TM (Bis(2-ethylhexyl thioglycolate) dioctyltins)	tin (organic)	Boryszew Erg S.A.

- Polanvil S-67 suspension poly(vinyl chloride), Anwil S.A., Włocławek ( $M_w = 129\,300$ ,  $M_n = 99\,600$ ),
- titanium whites – type R-210 and R003, „Police” Chemicals S.A.

### Sample Preparation and Formulation

The test samples in the form of film (Tab. 2-3) were obtained by weighing certain

quantities of PVC, stabilizer and titanium dioxide and homogenizing them initially in a mortar. Afterwards, 25 ml of tetrahydrofuran (THF) were added to 6 g of each sample and heated on a hot plate for 10 – 15 minutes while stirring the content. The suspensions were poured into 10cm diameter Petri dishes and left for 24 hours at ambient conditions for the solvent to evaporate and obtain the film.

**Tab. 2. PVC compound with R-210 white**

Sample code	PVC	TiO <sub>2</sub>	Stabilizer	Composition a/b/c, grams
	a	b	c	
A1	S-67	R-210	calcium-zinc (1)	9/0,5/0,5
A2				9/0,66/0,33
B1			calcium-zinc (2)	9/0,5/0,5
B2				9/0,66/0,33
C1			lead (inorganic)	9/0,5/0,5
C2				9/0,66/0,33
D1			lead (inorganic-organic)	9/0,5/0,5
D2				9/0,66/0,33
E1			lead (organic)	9/0,5/0,5
E2				9/0,66/0,33
F1			tin (organic)	9/0,5/0,5
F2				9/0,66/0,33
Reference sample 1	S-67	R210	–	9/1

**Tab. 3. PVC compound with R003 white**

Sample code	PVC	TiO <sub>2</sub>	Stabilizer	Composition a/b/c, grams
	a	b	c	
G1	S-67	R-003	calcium-zinc (1)	9/0,5/0,5
G2				9/0,66/0,33
H1			calcium-zinc (2)	9/0,5/0,5
H2				9/0,66/0,33
I1			lead (inorganic)	9/0,5/0,5
I2				9/0,66/0,33
J1			lead (inorganic-organic)	9/0,5/0,5
J2				9/0,66/0,33
K1			lead (organic)	9/0,5/0,5
K2				9/0,66/0,33
L1			tin (organic)	9/0,5/0,5
L2				9/0,66/0,33
Reference sample 2	S-67	R003	–	9/1



## Tests method

### Visual assessment

The intensity of the color changes caused by UV radiation in the presence of water/HCl solution were assessed visually according to the accepted scale (Image 1):

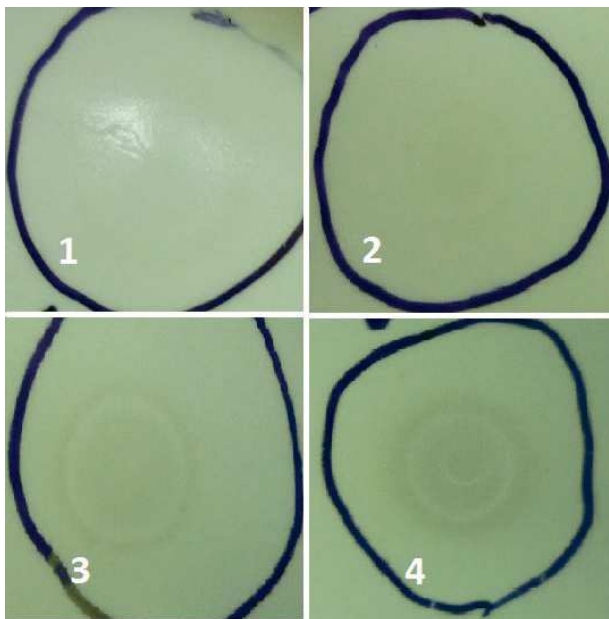


Image 1. Sample surface color change intensity scale in areas where water/HCl solution drops were applied and after exposure to UV radiation

0 – no change, 1 – barely perceptible change, 2 – perceptible change, 3 – clear change, 4 – very clear change, G – graying

Image 1 shows the proposed scale of sample surface change intensity.

The intensity of the color changes caused by UV radiation in the presence of water/HCl solution after application of H<sub>2</sub>S were assessed visually according to the accepted scale:

- 0 – no change,
- 1 – darkening (bronzing)
- 2 – apparent darkening (bronzing)

Determination of color change in accordance with RAL CLASSIC:

- RAL 1001 – beige
- RAL 1014 – ivory
- RAL 1015 – light ivory

RAL 1011 – brown beige

### FTIR Analysis

Infrared studies were performed using a Thermo Scientific Nicolet iS10 spectrometer. The spectra of the selected samples and the backgrounds were registered in the wave number range of 4000 – 600 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup> and a scan number of 32 using an ATR adapter fitted with a crystal diamond.

### Microscopic examinations

Changes in the color of the film in places where the water droplets or the HCl (1:1) solution were applied and subjected to UV radiation exposure for 5, 10, 20, and 30 min, were evaluated on the basis of images obtained under a Bresser Biolux 3,5" optical microscope at 100x magnification. Locations on the samples which were treated with an aqueous solution of hydrogen sulphide (for 3 mins), after having been exposed to UV radiation in the presence of distilled water, were also observed.

The surface appearance of PVC samples was evaluated on the basis of photos taken by a Hitachi SU8010 (Hitachi, Japan, 2011) scanning electron microscopy (SEM). All the samples were sputtered with a 7-8 nm layer of gold. Basic conditions for microscopic observation: detector type: SE (second electron), acceleration voltage: 2 kV, current: approx. 10 microamperes, so-called working distance: 8-9 mm.

## RESULTS AND DISCUSSION

The results of tests of the resistance of PVC samples to UV radiation and distilled water/aqueous solution of hydrochloric acid (1:1), and then to an aqueous solution of hydrogen sulphide, are presented in Tables 4-7. The color changes taking place on the surface of the test samples were evaluated with the naked eye.

All samples (containing Pb compounds) after being treated with an aqueous H<sub>2</sub>S solution, revealed areas, where distilled water/hydrochloric acid solution droplets were exposed to UV light. This most likely attests to the fact that the presence of trace amounts of Pb<sup>0</sup>, which

reacted with H<sub>2</sub>S to form PbS, dyed the surface of the samples in these areas.

**Tab. 4. Color changes of PVC samples containing R-210 white and different stabilizers caused by UV radiation in the presence of water/HCl solution**

Sample code	Changes in the color of the surface of the film in the droplet area							
	distilled water/exposure time, min.				aqueous solution of HCl (1:1)/exposure time, min.			
	5	10	20	30	5	10	20	30
A1, A2	0				0			
B1, B2	0				0			
C1	0				0			
C2	0			1G	0		2G	3G
D1	0	1G	1G	2G	2G	3G	3G	
D2	0	4G	4G	0			2G	
E1	0	1G	1G	0				
E2	0	1G	2G	0				
F1, F2	0				0			
Reference sample 1	0				0			

**Tab. 5. Color changes of PVC samples containing R003 white and different stabilizers caused by UV radiation in the presence of water/HCl solution**

Sample code	Changes in the color of the surface of the film in the droplet area							
	distilled water/exposure time, min.				aqueous solution of HCl (1:1)/exposure time, min.			
	5	10	20	30	5	10	20	30
G1, G2	0				0			
H1, H2	0				0			
I1	0			2G	0	2G	3G	
I2	0	1G	2G	0	2G	2G		
J1	0	1G	4G	4G	0	1G	2G	
J2	0	2G	3G	0				
K1, K2	0				0			
L1, L2	0				0			
Reference sample 2	0				0			

**Tab. 6. Color changes of PVC samples containing R-210 white and different stabilizers, induced by UV radiation in the presence of water/HCl solution following treatment with H<sub>2</sub>S**

Sample code	Changes in the color of the surface of the film in the droplet area							
	distilled water / exposure time, min.				aqueous solution of HCl (1:1) / exposure time, min.			
	5	10	20	30	5	10	20	30
A1, A2	0				0			
B1, B2	0				0			
C1	1, R1014				1, R1014			
C2	1, R1014				1, R1014			
D1	2, R1011				1, R1001			
D2	2, R1011				2, R1011			
E1	1, R1001				1, R1001			
E2	1, R1001				1, R1001			
F1, F2	0				0			
Reference sample 1	0				0			

**Tab. 7. Color changes of PVC samples containing R003 white and different stabilizers, induced by UV radiation in the presence of water/HCl solution following treatment with H<sub>2</sub>S**

Sample code	Changes in the color of the surface of the film in the droplet area							
	distilled water / exposure time, min.				aqueous solution of HCl (1:1) / exposure time, min.			
	5	10	20	30	5	10	20	30
G1, G2	0				0			
H1, H2	0				0			
I1	1, R1014				1, R1014			
I2	1, R1001				1, R1014			
J1	2, R1011				2, R1011			
J2	2, R1011				2, R1011			
K1	1, R1015				1, R1015			
K2	1, R1015				1, R1015			
L1, L2	0				0			
Reference sample 2	0				0			

On the basis of tests carried out as part of blind trials, it was shown that PVC/TiO<sub>2</sub> com-

positions (without thermal stabilizers) treated with UV/H<sub>2</sub>O and UV/HCl, do not undergo graying.

#### FTIR Analysis

Figures 1-3 present the FTIR spectra of the surfaces of samples D2, I1, and J1 (containing lead stabilizers) in places exposed to UV radiation and water/HCl solution/H<sub>2</sub>S solution.

The spectra of these samples in places with no color change, grey spots and darkening, are very similar to each other. The color changes on the surface of the samples were reflected in the FTIR spectra in the form of small changes in the absorption band layout in the wave range of 1050-1800 cm<sup>-1</sup>. In the spectrum of sample D2 at the UV light/water/H<sub>2</sub>S exposure area, the 1730 cm<sup>-1</sup> carbonyl group band became sharper, there was a reduction in the intensity of the 1080 cm<sup>-1</sup> band, whereas the 1480 cm<sup>-1</sup>

band almost completely vanished. Furthermore, additional, previously absent, low intensity 1580 cm<sup>-1</sup> and 1530 cm<sup>-1</sup> bands appeared. In the case of sample I1, the difference involved only a slight sharpening of the 1730 cm<sup>-1</sup> band at the UV/HCl/H<sub>2</sub>S exposure location. In the spectrum of sample J1, there was a sharpening of the 1730 cm<sup>-1</sup> band at UV /water/H<sub>2</sub>S exposure location, the formation of an additional 1745 cm<sup>-1</sup> band and a lowering of the baseline at the UV/water and UV/water/H<sub>2</sub>S exposure location in relation to the place exposed only to UV light. In addition, the 1480 cm<sup>-1</sup> and 1080 cm<sup>-1</sup> bands (characteristic for PbSO<sub>4</sub>) have a lower intensity at the UV/water/H<sub>2</sub>S exposure location.

#### Microscopic examinations

Images 2-7 show the microscopic images of the test samples. Image 2 shows a fragment of

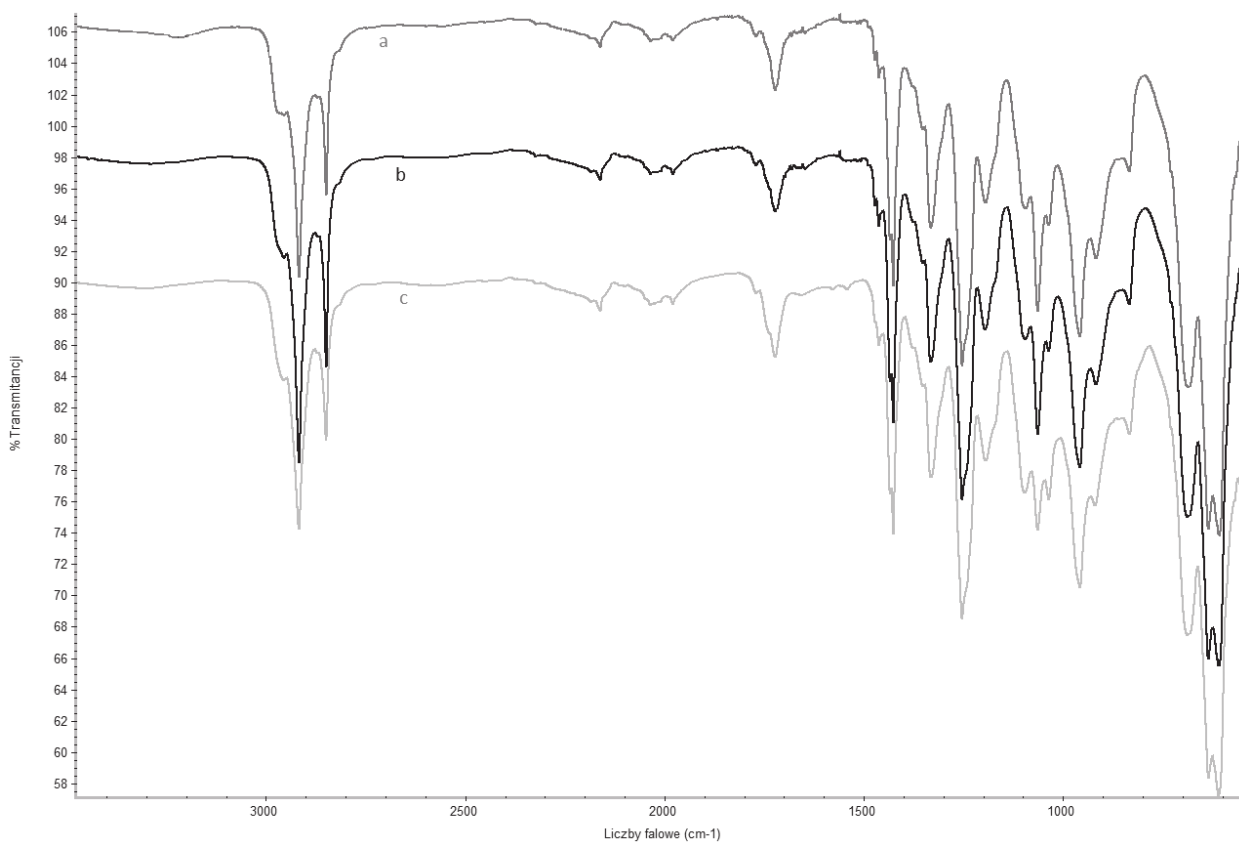


Fig. 1. FTIR spectra of D2 sample-place exposed to UV radiation for 30 minutes (a), place exposed to UV radiation for 30 minutes and water-gray stain (b), place exposed to H<sub>2</sub>S solution after exposure to UV radiation for 30 minutes and water-darkening (c)



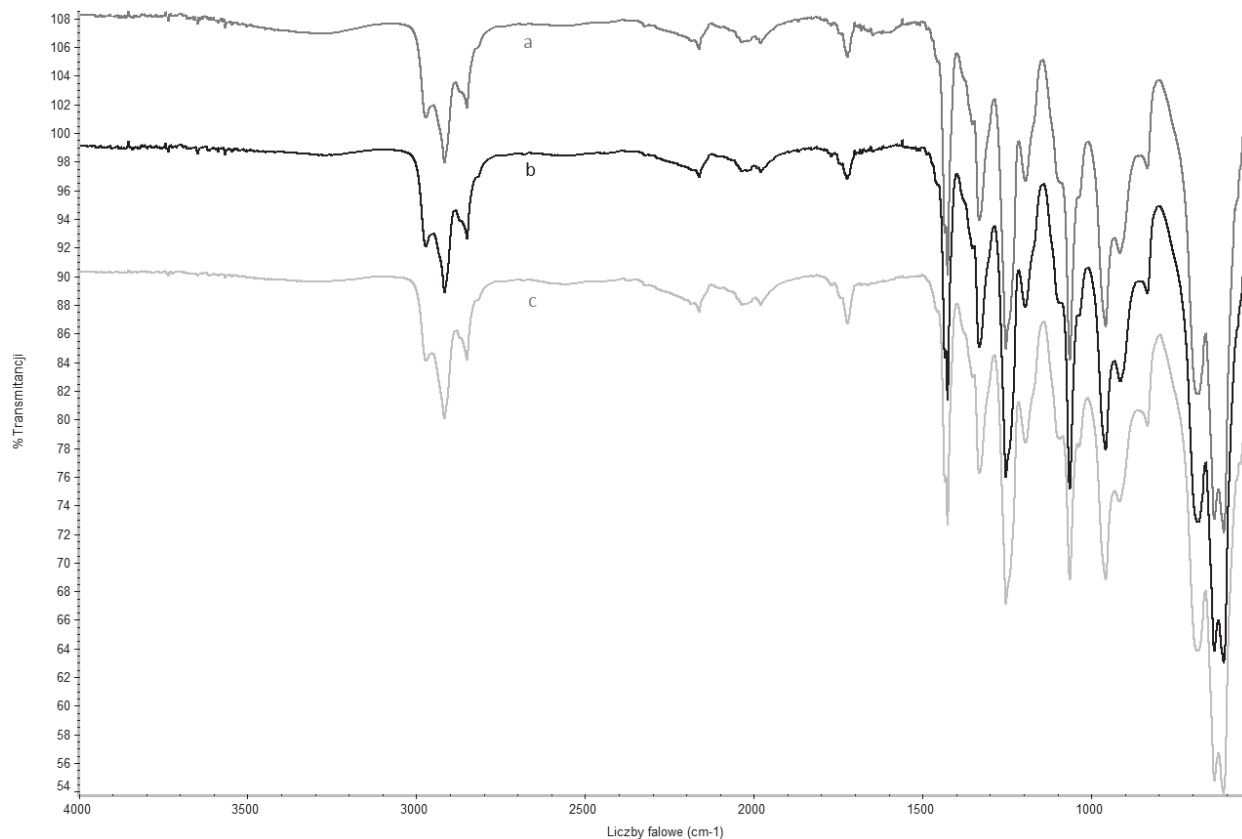


Fig. 2. FTIR spectra of I1 sample-place exposed to UV radiation for 30 minutes (a), place exposed to UV radiation for 30 minutes and HCl-gray stain (b), place exposed to H<sub>2</sub>S solution after exposure to UV radiation for 30 minutes and HCl-darkening (c)



Image 2. SEM image – fragment of J1 sample surface exposed to UV radiation without the presence of H<sub>2</sub>O

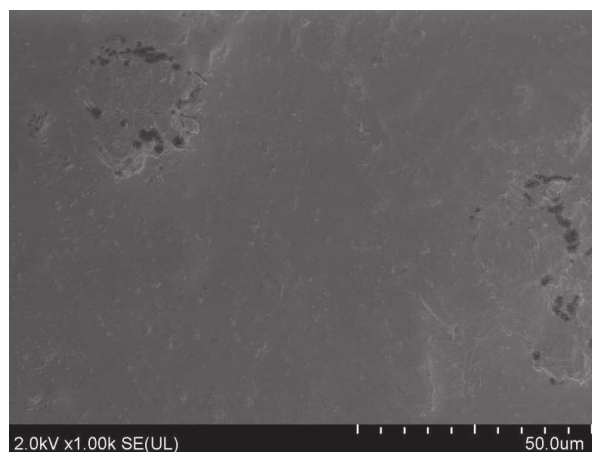


Image 3. SEM image – a fragment of the surface of sample J1, on which a droplet of distilled water was applied and which was then exposed to radiation

the J1 sample surface exposed to UV radiation without the presence of H<sub>2</sub>O, with visible TiO<sub>2</sub> agglomerates and stabilizers in the PVC matrix. Images

3-5 show fragments of the surfaces of samples J1 and I2, on which distilled water droplets were

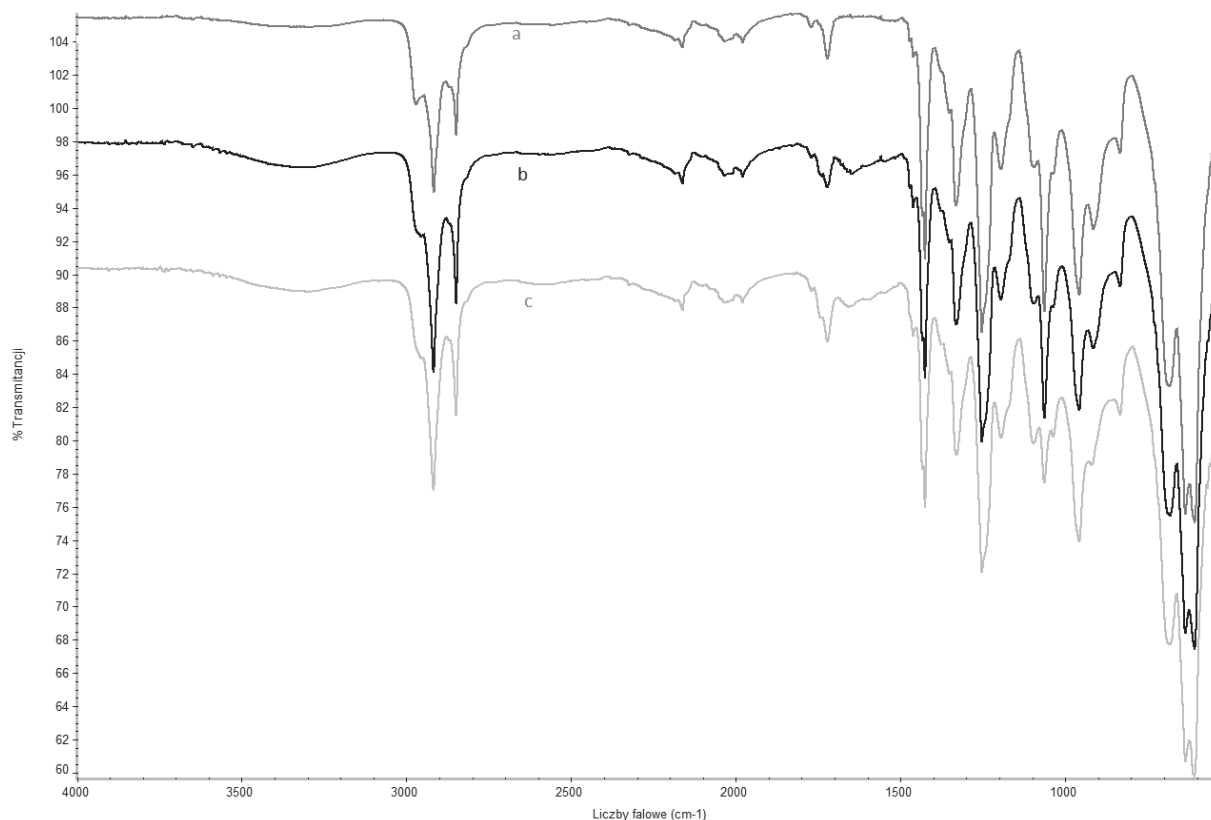


Fig. 3. FTIR spectra of J1 sample-place exposed to UV radiation for 30 minutes (a), place exposed to UV radiation for 30 minutes and water-gray stain (b), place exposed to  $H_2S$  solution after exposure to UV radiation for 30 minutes and water-darkening (c)

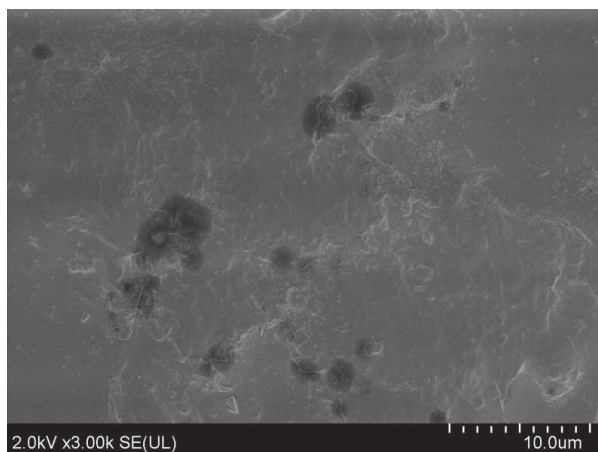


Image 4. SEM image – a fragment of the surface of sample J1 with visible dark areas formed most probably as a result of the presence of  $Pb^0$

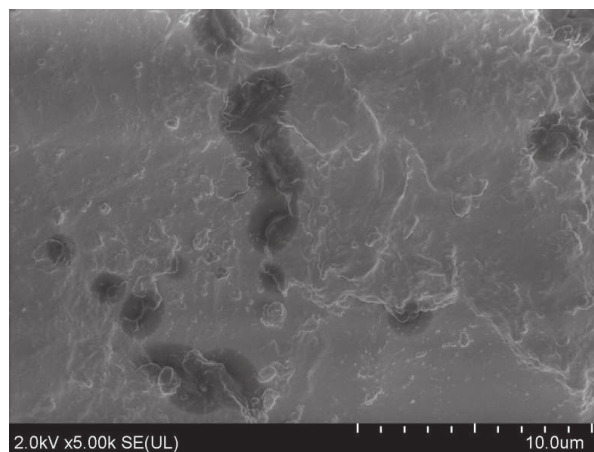


Image 5. SEM image – a fragment of the surface of sample I2 with visible dark areas where  $Pb^0$  most likely appeared

applied and which were then exposed to UV radiation. Dark spots are visible in places where a reduction of  $Pb^{2+}$  to  $Pb^0$  occurred.

It is believed that the areas in which a reduction of  $Pb^{2+}$  to  $Pb^0$  took place, are seen under the microscope as a series of scattered dark



Image 6. Grey area on J1 sample in place of application of water droplets after UV exposure for 30 minutes followed by exposure to an  $H_2S$  solution.

„spots”. A collection of these local dark areas creates a picture of grey spots observed with the naked eye on the test samples.

After a solution of hydrogen sulphide was applied in the area, which was previously activated by UV radiation in the presence of water, the gray spot observed earlier darkened. Visible dark-brown spots in the areas where water droplets were applied and then exposed to UV radiation for 30 minutes and afterwards to an  $H_2S$  solution, are most probably made up of lead sulphide (see image 6, sample J1).

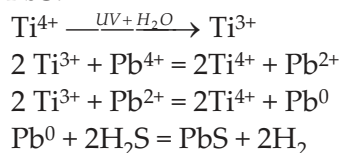


Image 7. Area of sample J1 where water droplets were applied and which was exposed to UV radiation for 20 minutes and then to a solution of  $H_2S$  (left side) and UV radiation for 30 minutes (right side)

However, in the area which was activated by UV radiation in the presence of water, and which was not exposed to hydrogen sulphide, the dark spots are not visible (see left side of image 7).

In work attempting to explain the causes of the graying of  $TiO_2$  tinted PVC components, two options of how this phenomenon has come to be are taken into account. According to Gesenhues [19,20], the graying of lead-compound stabilized PVC is caused by the surface reduction of  $TiO_2$ , the condition of which returns to initial state, when the pigment is exposed to the air in the later stages of PVC degradation. However, the work does not explain why the surface reduction of titanium white concerns PVC compositions containing Pb compounds. Also, this phenomenon did not take place in the case of stabilization with Ca/Zn. Our work, however, did not confirm this theory, as the explored PVC/ $TiO_2$  compositions (without thermal stabilizers) exposed to UV/ $H_2O$  and UV/HCl did not undergo graying.

In turn, Lemaire et.al. [13, 14, 23] suggested that this process is initiated by a reduction of  $Ti^{4+}$  to  $Ti^{3+}$  by the action of UV in the presence of water and, at the same time, is assisted by a reduction or decomposition of lead compounds, which includes the formation of metallic lead ( $Pb^0$ ). This explanation seems to confirm previous experimental results, as well as our observations, as only the samples containing lead stabilizers underwent graying. For places on which surface graying was invoked artificially and  $H_2S$  solution droplets were applied, these places turned a clearly darker color, which can be explained by the formation of  $PbS$ .



Furthermore, a spectroscopic analysis of the selected samples (D 2, I 1, J 1) which were exposed to UV and an  $H_2S$  solution, showed that the absorption bands at wavenumbers

1080  $\text{cm}^{-1}$  and 1480  $\text{cm}^{-1}$ , have a lower intensity in relation to the corresponding absorption bands of the sample exposed only to UV radiation. These bands are characteristic for  $\text{PbSO}_4$  and a decrease in their intensity in the spectra might indicate a smaller mass share of lead in the form of sulfate on the surface of the samples. Unfortunately, the fact that PbS is formed cannot be confirmed by means of infrared spectroscopy, since this compound absorbs infrared radiation in the range of wavenumbers 4000-600  $\text{cm}^{-1}$ .

On the basis of the tests carried out it has been shown that the type of thermal stabilizer used plays an important role in artificially invoking PVC sample graying. Grey discoloration appears only when Pb stabilizers are used in the PVC composition, and it is probably the result of the impact of  $\text{TiO}_2$  and lead compounds, which were previously activated by UV radiation. It was found that a change in color occurs only in locations where  $\text{H}_2\text{O}$  droplets were applied, which may attest to the catalytic action of water in the process. Therefore, PVC sample graying in the initial phase of surface degradation of the polymer, also confirms that  $\text{Pb}^{4+}$  ions play a key role in the process, as also suggested in the work by Lemaire [23].

To sum up, it can be concluded that titanium white, lead compounds and water are important factors contributing to the graying of PVC products exposed to UV radiation.

The simulation method proposed in the work, enables quick verification of the possibility of this phenomenon occurring for a given formulation of a PVC composition.

This method makes it possible to invoke graying artificially and is most likely to correspond to the observations of the natural aging process.

Although the proposed method of preparation of samples used to evaluate the impact of UV radiation and the presence of water on the color change of a PVC/ $\text{TiO}_2$ /thermal stabilizer composition, it does not provide the optimal degree of dispersion of additives in the polymer matrix. However, it is simple and useful in

assessing the possibility of the occurrence of graying.

The tests conducted have made it possible to clarify the causes of the surface graying of PVC parts used in outdoor conditions.

## CONCLUSIONS

On the basis of the studies, it is concluded that:

1. Graying of PVC parts under the action of UV radiation occurs only when lead stabilizers are used.
2. Discoloration occurs neither when tin nor Ca/Zn stabilizers are used in the PVC compositions.
3. Only places which come into contact with  $\text{H}_2\text{O}$  during UV irradiation turn grey, which proves that water plays a catalytic role in the surface graying of PVC elements.
4. The grey discoloration of PVC products, exposed to UV radiation (in the presence of water), which are stabilized by lead compounds containing  $\text{TiO}_2$ , is probably due to the reduction of  $\text{Pb}^{+4}$  to  $\text{Pb}^0$ .
5. The chloride ions present in an aqueous solution of HCl do not affect the appearance or absence of grey discoloration in PVC/thermal stabilizer/ $\text{TiO}_2$  systems. Therefore, the HCl formed in the initial stage of PVC degradation does not influence the appearance or the intensity of the grey areas, however, the further process of degradation associated with the formation of polyene bonds, leads to the pinking of the surface of a PVC product.
6. Treatment of the surface of PVC samples with an  $\text{H}_2\text{S}$  solution in the area of UV/ $\text{H}_2\text{O}$  and UV/HCl exposure allows for a preliminary determination of the likelihood of the occurrence of graying.
7. PVC/ $\text{TiO}_2$  compositions (without thermal stabilizers) exposed to UV/ $\text{H}_2\text{O}$  and UV/HCl do not undergo graying.
8. There was no impact of the  $\text{TiO}_2$  types used in the tests on the occurrence of grey discoloration and its intensity.



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