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UV-curable coatings – environment-friendly solution for sustainable protection of metal substrates

Powłoki utwardzane promieniowaniem UV – przyjazne dla środowiska rozwiązanie w zakresie trwałej ochrony podłoży metalowych

Providing adequate protection of metal materials is still a real challenge, which seems to be a twice as hard task, not only because of technical problems but also because of the requirements including the ecological aspect of the proposed solutions. Interesting alternatives to traditionally used paint coatings are undoubtedly UV-curable varnishes. Due to a number of advantages, among which the reduction of volatile organic compounds emissions or the renewable nature of the raw materials used for their production should be brought up, UV varnishes are relevant to classify them to so-called green chemistry. This article contains a brief description of the types and functions of individual components used in UV-curing formulas. The cross-linking mechanisms of such coatings were presented. A short review of the current state of the art in the field of obtaining new components for UV formulas and scientific reports on cross-linked protective coatings, including anti-corrosive ones, has been prepared. A tabular data presentation of UV-cured materials dedicated to application on metal substrates, which are currently commercially available was created. The synergic growth in the number of publications on the above matter and the constantly increasing register of UV raw materials suggest that in the coming years – due to its high attractiveness – this area will continue to gain in popularity.

Keywords: protective coatings on metal, UV-curable varnishes, green chemistry

Zapewnienie należytej ochrony materiałom metalowym wciąż stanowi wyzwanie, i to nie tylko z powodu problemów technicznych, lecz także ze względu na wymagania dotyczące ekologiczności proponowanych rozwiązań. Interesującą alternatywą dla tradycyjnie stosowanych pokryć malarskich są lakiery utwardzane promieniowaniem UV. Z uwagi na to, że mają wiele zalet, wśród których należy przede wszystkim wymienić redukcję emisji lotnych związków organicznych oraz odnawialny charakter surowców używanych do ich produkcji, lakiery UV doskonale wpisują się w koncepcję tzw. zielonej chemii. W artykule opisano rodzaje i funkcje poszczególnych komponentów stosowanych w kompozycjach utwardzanych promieniowaniem UV. Przedstawiono mechanizmy sieciowania takich powłok. Dokonano krótkiego przeglądu aktualnego stanu wiedzy w zakresie otrzymywania nowych składników formuł UV oraz badań gotowych pokryć ochronnych, w tym antykorozyjnych. W ujęciu tabelarycznym przedstawiono informacje na temat obecnie dostępnych w sprzedaży komercyjnej materiałów utwardzanych promieniowaniem UV przeznaczonych do aplikacji na podłoża metalowe. Coraz większa liczba publikacji w tym zakresie oraz stale rozrastająca się baza surowców UV pozwalają sądzić, że w najbliższych latach tematyka ta będzie zyskiwać na popularności.

Słowa kluczowe: powłoki ochronne na metal, lakiery utwardzane promieniowaniem UV, zielona chemia

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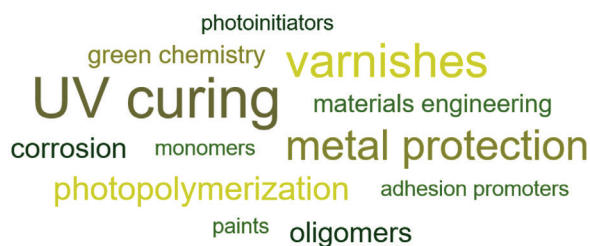
Fig. 1. UV-curable varnishes for metal substrates – keywords cloud

Rys. 1. Lakiery utwardzane UV na podłoża metalowe – chmura słów kluczowych

Fig. 2. The number of papers published in the past decade including keywords "UV-curable coatings" and "anti-corrosive coatings"

Rys. 2. Liczba opublikowanych w ostatniej dekadzie prac zawierających słowa kluczowe „powłoki utwardzane UV" oraz „powłoki antykorozyjne"

1. Introduction

Varnishes cured by UV radiation are an interesting alternative to traditionally used coating solutions. Free of volatile organic compounds (VOCs), produced in compact devices, they perfectly fit into the concept of the so-called green chemistry [1]. The high content of solid parts in UV formulas enables the application of thin coatings, which, depending on the purpose, can be applied to a wide range of surfaces e.g. wood, paper or glass [2–4]. Their attractiveness is also reflected in the satisfactory efficiency of the application process, resulting directly from the waste-free nature of this technology and the fact that the transformation of the liquid phase (initial composition) into the solid phase (polymerization product) takes place in a very short time, even within a few seconds. The main advantages of UV technology application are very high production capacity, short time exposure, the abovementioned lack of emissions of VOCs, toxic and flammable organic compounds into the atmosphere and an easily controlled polymerization process including curing temperature [5]. The disadvantages of this technique are the possibility of curing only relatively thin layers, preferably non-pigmented (especially cationic cross-linked compositions), which results from partial absorption of light during cross-linking of coatings and the phenomenon of oxygen inhibition – oxygen quickly reacts with radicals located on the carbon atom to form very few reactive peroxide radicals, which can slow down or even stop the polymerization process. Despite the inconveniences related to the thickness of the cured coating, obtaining the right color and the phenomenon of yellowing, it is possible to radically cross-link UV coatings containing pigments [6].

The UV curing technology market has been growing dynamically in recent years. An important reason for the development of this technology is its unique process characteristics and the related economic aspect, the increasing availability of raw materials needed to formulate liquid coating compositions and the existing restrictions related to, among others, waste management [7]. The subject of UV-cured coatings has a high application potential, especially in terms of the use of renewable raw materials and renewable energy sources [8].

This article presents the current state of the art of UV-curable varnishes dedicated to metal substrates. The overview of literature and solutions found in the industry was performed with the use of meticulously selected main keywords based on commonly known research databases i.e. Google Scholar and ScienceDirect. Data comes from information brochures and websites of manufacturers and distributors of raw materials for paints and varnishes formula-
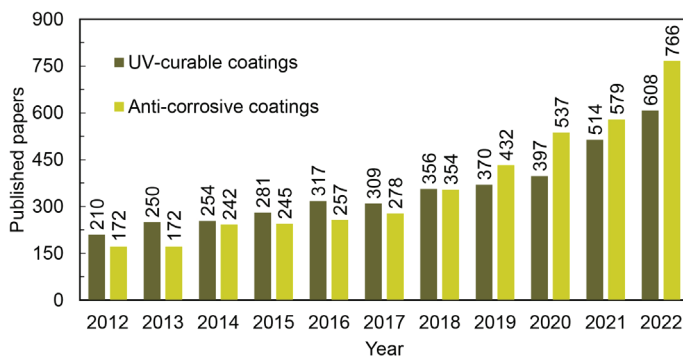
tion were also used. The cloud containing chosen words connected with the presented subject is shown in Fig. 1. The abovementioned keywords were useful in the process of preparing this work.

Based on the literature analysis on the topics of light-cured coatings on metal and protective coatings with anti-corrosive properties, a graph showing the number of published papers as a function of years was drawn up (interval between 2012 and 2022; Fig. 2). It can be observed that from year to year, the number of papers focused on this topic is increasing. The registered growth is clear and allows to assume that the visible trend will continue for several more years. Thus, for the keywords "UV-curable coatings" and "anti-corrosive coatings" in the past decade, the number of published papers has increased from 210 to 608 and from 172 to 766, respectively, which correspond to a nearly threefold and more than fourfold increase. The collected data clearly shows that the discussed topic is still important, moreover, it is increasingly popular. It can be presumed that this trend corresponds primarily to efforts to find environmentally friendly solutions that may have the potential to be implemented in industry. Wherein, the observed increase relates primarily to published scientific reports. In the case of industrial solutions, in recent years this trend is not as visible as over the past decades. More and more is being said about the reduction of organic solvents usage and application of water-based binders, as well as decreasing the share of zinc dust – especially in the context of anti-corrosive coatings. These transformations will take many years, nevertheless, it is worth taking up the challenge and following their progress.

2. Cross-linking of coatings in the process of irradiation with UV radiation

UV radiation is only a small part of the complete spectrum of electromagnetic radiation (Fig. 3). Radio waves and microwaves have a long-wave spectrum. Infrared, visible and UV light, on the other hand, have a short-wave spectrum. The wavelength range of UV radiation includes three main ranges, which are characterized by the different abilities to cross-link varnish products. UV-C, covering the range of 200÷280 nm, causes direct consolidation of light-curing varnishes and is used for surface hardening. UV-B, which covers the range of 200÷315 nm, penetrates deeper into the varnish layer, thanks to which it provides deep hardening of the coating. UV-A, in the range of 315÷380 nm, penetrates into the deepest layers of varnish, enabling the hardening of thick coatings and even those containing pigments [9].

Photochemically initiated polymerization is a chain reaction started by free radicals or ions formed in the process of
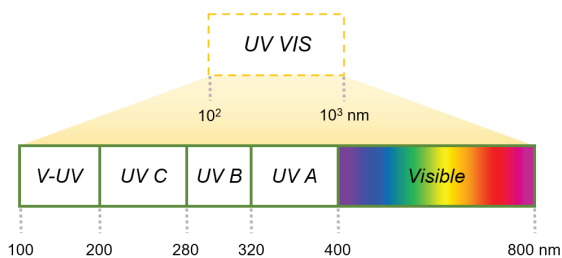
Fig. 3. Electromagnetic spectrum

Source: [10, p. 7].

Rys. 3. Widmo fal elektromagnetycznych

Źródło: [10, s. 7].

Fig. 4. The general UV-crosslinking of polymer coating process illustration

Rys. 4. Schemat przebiegu procesu sieciowania powłok polimerowych promieniowaniem UV

where: R – oligoester, oligoether, oligourethane, oligosiloxane, BPA derivatives; R$_1$ – H, CH$_3$

Fig. 5. The general structure of the oligomer component

Rys. 5. Ogólna struktura oligomeru

irradiation with visible or ultraviolet light. This process, commonly referred to simply as photopolymerization, is sometimes also called photocrosslinking in relation to systems containing multifunctional monomers. As mentioned earlier in the article, the photopolymerization of the varnish is accompanied by the transformation of the liquid composition in the initial state into a cross-linked solid state polymerization product. The duration of polymerization is influenced by both the chemical nature of the raw materials used and their mutual ratio. The general scheme of the cross-linking process of polymer coatings induced by UV radiation is shown in Fig. 4. In the photopolymerization of multifunctional monomers, elementary reactions of initiation, propagation and termination are also distinguished. The growth of the polymer chain can occur by the addition of a new monomer molecule or by the reaction of the active site with the unsaturated bond of the side group, creating a branched structure. This reaction leads to an increase in the density of the forming polymer network [10, 11].
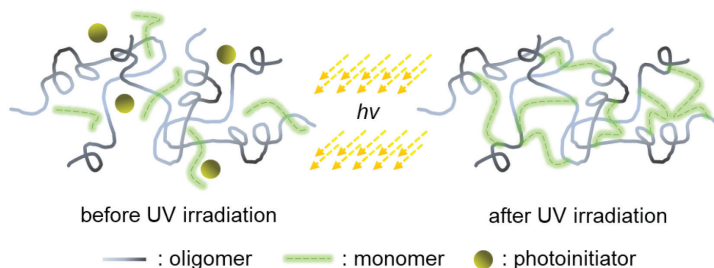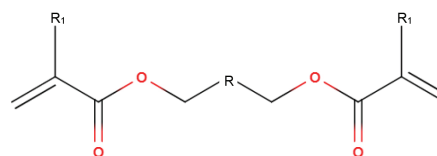
3. Raw materials used in UV curing compositions

3.1. General information about UV raw materials

As in the case of formulation of paints and varnishes, obtaining coating compositions cured by UV radiation requires the combination of appropriate raw materials, which can be assigned to several basic groups. Thus, the composition of the UV-cured coating usually includes [12]:

Table 1. Classes of oligomers
Tabela 1. Rodzaje oligomerów

Classes of oligomers (radiation curable binders)	Description
Acrylated polyesters	These materials cover a broad range of viscosities (mostly low) and reactivities. They are cheaper in comparison to other acrylated prepolymers and have satisfactory compatibility with other prepolymers. When the molecular weight is lower, a reduction in reactivity and increased surface inhibition are observed (monomer-like behavior). Change in the molecular weight leads to obtaining oligomers with viscosity from low even to hard solids at room temperature
Acrylated epoxies	They are versatile in the use with a high cure rate and can be formed in the reaction of an epoxy group with acrylic or methacrylic monomers. Acrylated epoxidized oils have low viscosity, satisfactory pigment wetting properties and good flexibility. Cross-linked epoxy novolac acrylates have better strength properties than standard epoxy acrylates
Acrylated urethanes	As well as urethanes, acrylated urethanes are characterized by high chemical resistance, hardness and light stability. Can be obtained in a low-temperature reaction between hydroxyl and isocyanate groups without releasing volatile compounds. In such materials, chain extension by attaching a long chain diol may increase the flexibility of acrylated urethanes
Acrylated silicones	They exhibit resistance to heat and weather, with excellent flexibility and extensibility properties and are sensitive to air inhibition. Normally, they are cured in an inert atmosphere
Acrylated polyethers	In order to avoid degradation of the polyether bonds, the trans-esterification technique is used to acrylate the polyethers. Insertion of polyether linkages into an acrylated system is possible by the reaction with the isocyanate groups (elimination of problem with the removal of trans-esterification by-products). They are inexpensive to prepare and have lower viscosity compared with the polyester resins
Acrylated oils	Acrylated oils are derived from natural-origin materials, e.g. soybean, castor or fish oils, all of them contain triglyceride oils and are acrylated with acrylic acid similarly to epoxy acrylate manufacturing. They have a lower viscosity than epoxy acrylate, so there is no need to reduce it with reactive diluent. They are predominantly flexible, have an aliphatic acrylic backbone and low level of acrylic unsaturation
Thiolene systems	Thiolene systems are obtained in the process of free radical addition of mercaptans to olefins. Thiol/polyene systems are non-air inhibited and are characterized by low viscosity without the use of a diluent and are flexible in a cross-linked state. Polyfunctional thiol compounds applied as coatings have abrasive-resistant properties

Source: own study based on [12, 13].

Źródło: opracowanie własne na podstawie [12, 13].

Table 2. Classes of diluents/monomers
Tabela 2. Rodzaje rozcieńczalników/monomerów

Classes of diluents/monomers		Description
Vinyl based diluents	styrene and its derivatives	They are inexpensive, characterized by high hardness, quite volatile, cross-linked at a low speed. Compatible with many resins and monomers. It has been used in the case of unsaturated polyesters, and a less toxic alternative is currently being sought
	vinyl acetates	They are quite volatile and ignite easily, characterized by low chemical resistance, including to water. Excellent reducing agents
	N-vinylpyrrolidone	Despite that N-vinylpyrrolidone does not have an acrylate functional group in its structure, when used in the optimal molar ratio, it copolymerizes with acrylates. As an excellent reducing agent, it has been used for many years, but is now increasingly abandoned
Acrylic	monoacrylates	They have a wide range of properties depending on the type. Mostly volatile, with a strong odor and improved flexibility. Stands out: n-butyl acrylate (BA), 2-ethyl hexyl acrylate (EHA), iso decyl acrylate (IDA), isobornyl acrylate (IBA), 2-hydroxyethyl acrylates (HEA), 2-hydroxypropyl acrylate (HPA)
	diacrylates	They have a stronger odor than monoacrylates. They are irritating and carcinogenic. The main used area is in the production of UV adhesives. Stands out: 1,4-butanediol diacrylate (BDDA), 1,6-hexanediol diacrylate (HDDA), neopentyl glycol diacrylate (NPGDA), diethylene glycol diacrylate (DEGDA)
	triacrylates	Mainly used in printing areas. Stands out: pentaerythritol triacrylate (PETA), trimethylolpropane triacrylate (TMPTA)
	tetracrylates	A popular example of such a chemical compound is the low-volatility pentaerythritol tetraacrylate, which is used in many industries
	pentacrylates	A typical example of such materials is a fast-crosslinking, non-irritating dipentaerythritol (monohydroxy) pentaacrylate
Allylic monomers		Low-volatility triallyl cyanurate and trimethylolpropane trial ether can be distinguished
Plasticizing diluents		There are many types of plasticizing diluents, which are most highly volatile and can be used in formulations of solvent-borne paints. There are, among others butyl acetate or hexadecanol

Source: own study based on [12, 13].
Źródło: opracowanie własne na podstawie [12, 13].

— a high-viscosity prepolymer or oligomer that gives coatings basic physicomechanical properties,
— monomers that have two tasks: they are a non-volatile solvent/diluent of the resin and they are a reactant in the process of cross-linking the binder components,
— photoinitiators that absorb the energy of UV radiation and create free radicals that activate the polymerization process,
— other ingredients, i.a. pigments, fillers, defoaming agents, dispersing and wetting agents, matting agents etc., which improve the final properties of coatings.

3.2. Oligomers

Oligomers are raw materials that can be compared to polymers or resins in classic varnish products. The choice of the oligomer is critical as it directly influences the key properties of liquid and cross-linked UV curable compositions, such as: reactivity, gloss, adhesion to the substrate, chemical resistance, scratch and abrasion resistance, and yellowing. In order for a formulated varnish product to properly fulfill its function, it must be characterized by an appropriate combination of properties. When developing recipes for varnish products, their chemical structure, functionality and molecular weight should be taken into account.

It is worth mentioning that mixtures consisting of even several different oligomers are usually used to obtain UV formulas with the expected properties (provided they are mutually compatible). The general structure of the oligomer component is shown in Fig. 5. Classes of oligomers (radiation curable binders) with a short description of their chosen properties are shown in Table 1.

3.3. Diluents/monomers

Despite the great progress in the synthesis of new oligomers, a large part of the oligomers currently available on the market have too high viscosity, and therefore require dilution to be able to apply them using dedicated equipment. At the same time, it should be remembered that in order for the prepared formula to

maintain good reactivity, the use of monomers should be limited to a minimum. This is also related to the health aspect – the presence of unreacted monomer and possible by-products may cause skin irritations and allergies. As mentioned, acrylic monomers are used as reactive diluents and to give coatings specific properties (improvement of adhesion, chemical resistance, scratch resistance and others). Classes of diluents/monomers with a short description of their chosen properties are shown in Table 2. The chemical structures of selected acrylic monomers are shown in Fig. 6.

3.4. Photoinitiators

Photoinitiators are chemical compounds that, when irradiated with UV or visible light, are able to transform into reactive forms, i.e. free radicals, cations or anions, which initiate the polymerization of a liquid polymer composition. But anionic photopolymerization is not widespread on an industrial scale, rather in scientific reports. Like oligomers and diluents/monomers, they are the basic component of UV formulas that can be used in the production of protective and decorative coatings or adhesives. According to the mechanism of action, photoinitiators can be classified into radical and cationic photoinitiators. The former, in turn, are divided into Norrish type I or Norrish type II photoinitiators [12–14].

Norrish type I photoinitiators are characterized by the fact that during irradiation with UV radiation, the photoinitiator compound is split into two fragments which are free radicals with high reactivity (homolytic bonds are broken). Formed radicals are capable of initiating the polymerization process of the liquid UV formula. Type I photoinitiators are completely and irreversibly built into the polymer matrix. The mechanism of reaction with the use of Norrish type II photoinitiators is different from type I. In order for chemical compounds classified as type II photoinitiators to fulfill their function, they need a component that will be a source of hydrogen. The donors in this reaction are usually the so-called amine synergists. During the irradiation of type II photoinitiators, the hydrogen atom is detached from the synergist structure and
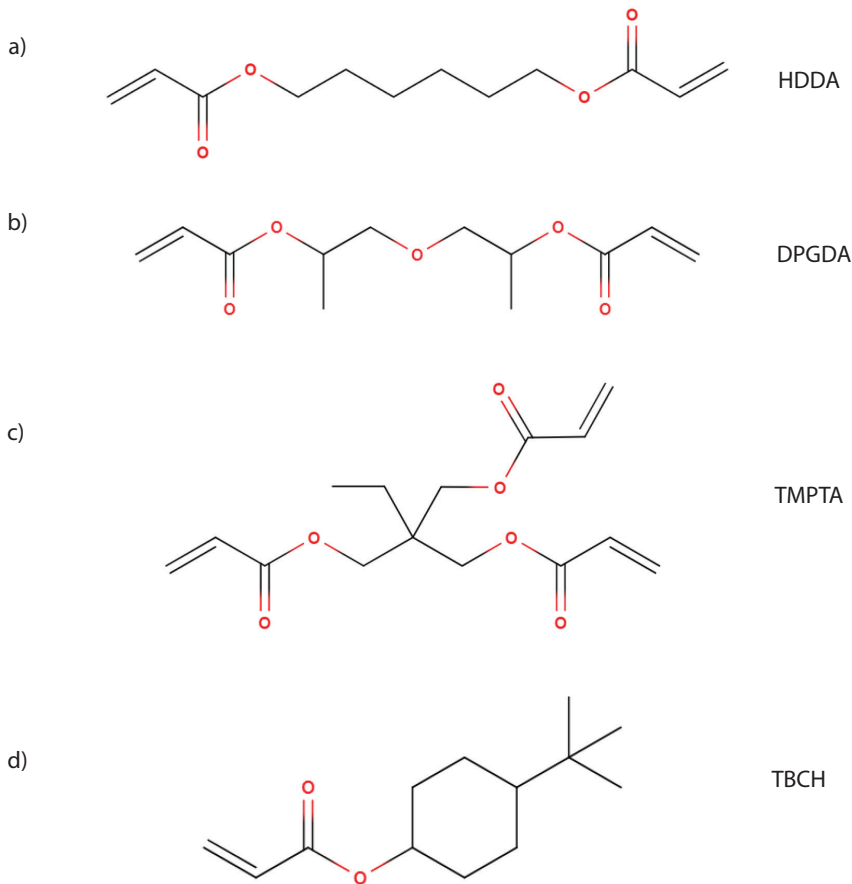
a)

HDDA

b)

DPGDA

c)

TMPTA

d)

TBCH

Fig. 6. Chemical structure of popular acrylic monomers: a) 1,6-hexanediol diacrylate (HDDA), b) dipropylene glycol diacrylate (DPGDA), c) trimethylolpropane triacrylate (TMPTA), d) 4-tert-butylcyclohexyl acrylate (TBCH)

Rys. 6. Struktura chemiczna popularnych monomerów akrylowych: a) diakrylan 1,6-heksanodiolu (HDDA), b) diakrylan glikolu dipropylenowego (DPGDA), c) triakrylan trimetylolopropanu (TMPTA), d) akrylan 4-tert-butylocykloheksylu (TBCH)

Norrish type I photoinitiators – cleavage
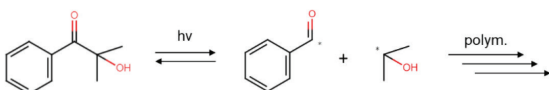
Norrish type II photoinitiators – abstraction
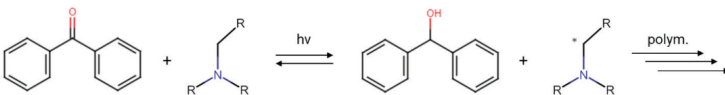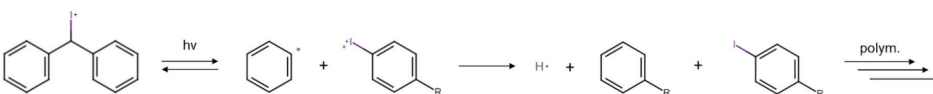
Cationic photoinitiators

Fig. 7. Mechanism of photopolymerization depending on the type of applied photoinitiator

Source: drawn on the basis [14].

Rys. 7. Mechanizm fotopolimeryzacji w zależności od rodzaju użytego fotoinicjatora

Źródło: opracowanie własne na podstawie [14].

free radicals are formed. They initiate the polymerization process of the liquid UV formula. The part comes from the synergist is incorporated into the polymer matrix. The third type of photoinitiators are cationic photoinitiators. Their mechanism of action is completely different from the previously described type I and II photoinitiators. The compounds included in this group are primarily iodonium and sulfonium salts. As in the case of type I photoinitiators, as a result of irradiation of these salts, the homolytic bondage is broken and free radicals are formed. The resulting free radicals react with the proton donor to Brønsted or Lewis acid. The acid formed in this reaction is the factor initiating the polymerization process of the liquid UV formula. Schemes illustrating the mechanism of photopolymerization using the described photoinitiators are shown in Fig. 7.

Appropriate selection of photoinitiators is very important for many reasons. First of all, it should be remembered that each of the photoinitiators is activated by a beam of light with a specific wavelength, therefore the photoinitiators used to formulate varnish products must be matched to the spectral characteristics of the lamp equipped in the curing chamber (high absorption in the emission range of the light source). Secondly, used photoinitiator affects the curing speed of the coating. Photoinitiators should form free radicals with high quantum efficiency and at the same time have a short lifetime to avoid inhibition by oxygen or monomer. The most important factors determining the choice of photoinitiators include: coating thickness, transparency or the presence of pigments and fillers, expected mechanical properties, odor, susceptibility to yellowing, degree of migration etc. Classes of photoinitiators with a short description of their chosen properties are shown in Table 3. The chemical structures of selected photoinitiators are shown in Fig. 8.

4. Recent advances in the synthesis of novel compounds for anticorrosive UV-curable coatings

As mentioned above, the subject of this review is of the moment, which is reflected in interesting papers published in recent years. Some of the recent studies covering mentioned

Table 3. Classes of photoinitiators
Tabela 3. Rodzaje fotoinicjatorów

Classes of photoinitiators	Description
Aromatic ketones and synergistic amines	As a result of hydrogen adsorption, benzophenone is photoreduced to benzopinacol in the presence of donors, which can be amino alcohols or N,N-dialkylamino benzene derivatives. The excitation of benzophenone to the singlet state occurs at a wavelength of 340 nm
Alkyl benzoin ethers	Improvement of benzoin yield is possible through alkylation reactions. Subjecting benzoins, benzoin alkyl ethers and alkylated benzoins to the Norrish type I reaction results in the formation of benzoyl radicals involved in the polymerization process
Thioxathones and derivatives	Thioxathane and its substituted compounds can be considered derivatives of benzophenone. They are used to produce thick, reflective coatings by pigmenting them with, for example, titanium white (TiO_2). Worth mentioning here: 2-chlorothioxanthone (2-CTX), and 2-isopropyl thioxantone
Benzil ketals	A representative of this group of photoinitiators worth mentioning is 2,2-dimethoxy 2-phenyl acetophenone (DMPA). This compound is classified as a type I photoinitiator. As a result of the decomposition of benzoyl and methyl radical, acetophenone is formed. Their stability is greater than that of benzoin ethers, they undergo yellowing quickly
Acylphosphine oxide	These compounds are characterized by high oxygen inhibition, which limits their reactivity during the curing of coatings. Mono-acylphosphine and bis- acylphosphine oxides are recommended for use in pigmented coatings as they have maximum absorption in the near UV and visible light range. They show a low tendency to yellowing of coatings
Ketoxime ester or acyloxime esters	Characteristic of these compounds is the Norrish type I cleavage reaction, which produces benzoyl and other radical, which then undergoes further cleavage
Acetophenone derivatives	One example that is considered a benzine ether is dialkoxy acetophenone. The main representative of this group is diethoxy acetophenone (DEAP), classified as Norrish type II photoinitiators. Chlorinated acetophenone derivatives are also used. The chlorine radical is considered to be extremely reactive, thanks to which it effectively initiates polymerization

Source: own study based on [12, 13].
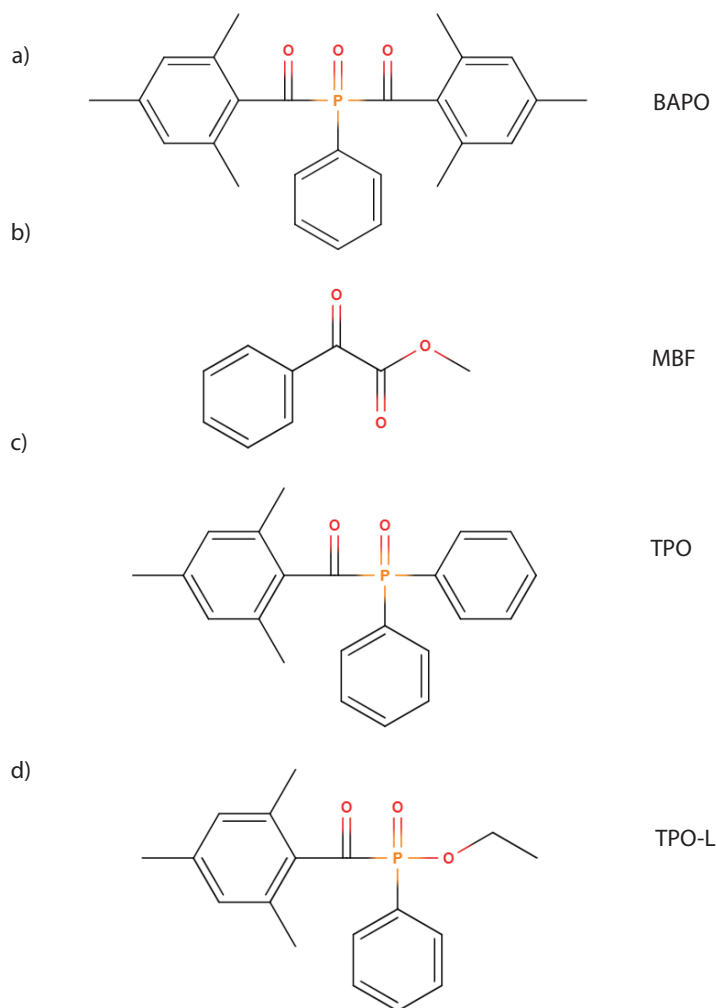Źródło: opracowanie własne na podstawie [12, 13].

Fig. 8. Chemical structure of popular photoinitiators: a) phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO), b) methyl benzoylformate (MBF), c) diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO), d) ethyl(2,4,6-trimethylbenzoyl) phenylphosphinate (TPO-L)

Rys. 8. Struktura chemiczna popularnych fotoinicjatorów: a) tlenek fenylobis(2,4,6-trimetylobenzoilo)fosfiny (BAPO), b) benzoilomrówczan metylu (MBF), c) tlenek difenylo(2,4,6-trimetylobenzoilo)fosfiny (TPO), d) etylo(2,4,6-trimetylobenzoilo)fenylofosfinian (TPO-L)

topics are presented below. Noè et al. [15] presented the research on the epoxidized epoxy oils from rose hip and grape seeds. Epoxidized rose hip and grape seed oils were mixed with the cationic photoinitiator – triarylsulfonium hexafluoroantimonate salts – and deposited on low-carbon steel plates. The films were subsequently crosslinked by UV light at room temperature. The corrosion protection effectiveness of the coatings was characterized by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements. It was shown that all of the tested coatings were able to provide good protection for the substrate. The best performance was provided by the epoxidized rose hip seed oils.

Another worth mentioning study on UV-curable anticorrosive coatings was proposed by Peng et al. [16] who introduced bio-mimetic leaf-like super-hydrophobic polymeric surfaces using UV-curing nanocasting technique. Here, the template from the surface of the natural leafs of *Xanthosoma sagittifolium* on polydimethylsiloxane (PDMS) was created by the thermal curing of PDMS pre-polymer. Then, epoxy-acrylate coatings with biomimetic structures were developed by the UV-radiation with a photoinitiator on cold-rolled steel electrodes using the prepared PDMS template. Prepared coatings are characterized by an excellent water-repelling performance (contact angle stated at 154°), which could significantly influence the anticorrosive properties of coatings.

In their study, Yu, Sahouani and Webster [17] synthesized a series of methacrylated bio-based resins for use in the formulation of UV-curable coatings on steel substrates. Here, methacrylated epoxidized sucrose soyate and dimethacrylated epoxidized sucrose soyate were synthesized from epoxidized sucrose soyate. Prepared resins were mixed with multifunctional reactive diluents and a photoinitiator and cured under UV light. Bio-based resin systems appeared to have a high

number of functional groups, and thus high crosslinked density was observed which also resulted in great solvent resistance and high hardness of discussed coatings.

In the research from Tong et al. [18], doped polyaniline (PANI) was added to UV-curable resin for the preparation of anticorrosive coatings. Photosensitive phytic acid (PAGA) was synthesized via the ring-opening reaction of glycidyl methacrylate and phytic acid. It was shown that PANI doped with PAGA improved the dispersion of PANI in coatings. What's more, the enhancement of adhesion was observed which was also reflected in the high anticorrosive performance confirmed with EIS and salt spray tests.

The effects of PANI doping were also tested by Jafarzadeh et al. [19] in a research on the synthesis of PANI reinforced with phosphoric acid (PhA). Composite coatings containing 0÷5 wt% of PANI doped with PA in a UV-curable polyester acrylate (PEA) resin were prepared and deposited on carbon steel. In the EIS measurements, it was observed that pure PEA coatings without PANI-PhA addition exhibit short-term barrier-type corrosion protection. The addition of 1÷3 wt% of PANI-PhA results in a remarkable enhancement of anticorrosive properties and provides long-term active protection of tested coatings. However, with the higher content of PANI-PhA (>3 wt%), the protective properties are lower, which is explained by the hydrophilicity of PANI that can lead to easier water transport and thus, the presence of weaker spots in the coatings.

Another work covering the topic of bio-based UV-curable coatings on metal was reported by Liu et al. [20]. Cardanol-based acrylate oligomers were synthesized via the ring-opening reaction between cardanyl glycidyl ether and polyacids. The acrylate oligomers were used for the formation of coatings on aluminum substrates and properties such as hardness, adhesion, chemical resistance or thermal stability were characterized. Obtained cardanol-based coatings appeared to be a perfect fit for metal substrates since the excellent hardness, adhesion and enhanced thermal properties were recorded. All this was reported while maintaining high bio renewable contents and, what's more, the possibility to use such a solution for anticorrosive systems.

Choi, Lee, and Ha [21] developed the synthesis route of UV-curable polyurethane acrylate oligomers using cycloaliphatic polyisocyanate and polycaprolactone polyol, polycarbonate polyol or cycloaliphatic polyester polyol. Proposed products were tested for the possibility of application as raw materials for pre-coated metal sheets which characterize by i.a. good corrosion after accelerated weathering tests and great chemical resistance in acidic, alkaline and water environments.

Another interesting topic in the area of UV-cured coatings are the insights on the synthesis of adhesion promotors which can have a beneficial impact on the anticorrosion performance of polymer coatings dedicated to metal. Wang et al. [22] developed a series of acrylated tannic acid with different acrylation degrees via the ring opening reaction of tannic acid (TA) and glycidyl methacylate (GMA) as bio-based adhesion promoters for UV-curable coatings on low-carbon steel and aluminum plates. The adhesion promotion effects on metal substrates were investigated via cross-hatch test and pull off analysis. Anticorrosion properties of the coatings were investigated by EIS and the salt spray test. It was proved that with the increasing acrylation degree, the adhesion promotion effect of TA-GMA enhanced firstly and then decreased. The highest adhesion promotion effect was observed for the TA : GMA molar ratio stated at 1 : 20. The corresponding results were reported for corrosion protection properties of coatings, indicating a high anticorrosion performance for discussed coating solutions.

In another work presented by this research group [23], the proposal for a unique preparation route of an eco-friendly adhesion promoter using natural compounds was given. The study was focused on a synthesis of phytic acid-based adhesion promoter with the photo-curable group. Here, a ring opening reaction of phytic acid (PA) and glycidyl methacrylate (GMA) in an aqueous solution was performed. Via the adjustment of the PA/GMA ratio, a series of adhesion promotors with different contents of photo-curable methacrylate group have been obtained. It was shown that, the developed PA-GMA improved the adhesion strength between UV-cured coatings and metal substrates which also reflected in the outstanding corrosion protection properties. Considering the facile preparation strategy, low-costs, and exceptional adhesion promoting performance, both of the abovementioned solutions can be promising for the application in UV-cured anticorrosive coatings.

In the research proposed by Millet et al. [24], the evaluation of the corrosion protection of UV-cured methacrylate-based coatings was done. The coatings containing diacrylate monomers as well as phosphonated methacrylate monomers were deposited on steel substrates and corrosion performance was assessed via EIS measurements. Primarily, the influence of the phosphonic acid methacrylate content on corrosion protection was investigated. Then a new phosphonated fatty acid (PFA), acting as an inhibitive component for the enhancement of corrosion protection, was synthesized and added to the formulation. This modification resulted in significant anticorrosive performance improvement which was explained by the inhibitive activity of PFA at the steel coating interface and by the improvement of the adhesion, and thus, also barrier properties.

Phalak et al. [25] synthesized a tri-functional acrylate monomer from ricinoleic acid (RA) and used as biobased reactive diluent with an oligomer for a UV curable coating application. Prepared diluents were added to the formulation in various concentrations (10÷30 wt%) and were applied on wood and metal panels. Solvent resistance as well as mechanical properties of UV-curing coatings were characterized. It was observed that with the increasing diluent concentration, properties such as tensile strength and modulus or pencil hardness are also increasing. The ability of discussed diluent to cure under UV light minimizes VOC emissions and can be considered as attractive replacement for petrochemical-based oligomeric UV cured coatings.

Fertier et al. [26] reported studies on a isosorbide as green monomer involved in a photopolymerization for UV-curable coatings. Modification of isosorbides with the use of (meth)acryloyl chloride was conducted in a one-step reaction processes and the influence of biobased monomers addition to the final formulations on the adhesion performance was tested. Segments of polycaprolactone (CAPDA) or poly(tetramethylene glycol) (PEGDA) were mixed with isosorbide diacrylates (ISDA) and tested in various mass ratios. The improvement of properties such as abrasion, gloss and adhesion in formulations with ISDA/PEGDA and ISDA/CAPDA with an addition of adhesion promoter was observed.

5. Industrial solutions

UV-curable coating technology has grown in popularity in recent years. The raw materials needed to formulate light-curable compositions are now easily attainable in the whole Europe, Asia and the US. Commercially available materials are offered by many manufacturers including: Allnex, IGM Resins, Rahn AG or Sartomer (Arkema). Various types of acrylates (oligomers) dedicated to metal coatings are distributed. Their viscosity is dependent on the chemical nature of the polymer, and, if necessary, can be reduced by the addition of suitable, low-viscosity reactive diluents – monomers. Conventionally used monomers are mainly abovementioned: dipropylene glycol diacrylate (DPGDA), 1,6-hexanediol diacrylate (HDDA), isobornyl acrylate (IBOA) and trimethylolpropane triacrylate (TMPTA). Among the photoinitiators most commonly found in industrial practice should be noted: phenylbis(2,4,6-trimethylbenzoyl)phosphine

Table 4. Examples of commercially available light-curing oligomers dedicated to metal substrates
Tabela 4. Przykłady dostępnych w sprzedaży komercyjnej światłoutwardzalnych oligomerów przeznaczonych do zastosowania na podłoża metalowe

Product	Distributor	Chemical character	Acid number [mg KOH/g]	Viscosity at 25°C [mPa · s]	Selected properties
EBECRYL® 242	Allnex	aliphatic urethane acrylate oligomer in 30% IBOA	N/A	~21 000	• excellent flexibility • good adhesion to metal • good corrosion resistance
EBECRYL® 3300	Allnex	modified BPA epoxy acrylate	≤1.5	750÷1100	• good adhesion, including metal substrates • good chemical and corrosion resistance • balanced hardness and flexibility
EBECRYL® 3416	Allnex	epoxy acrylate in 35% tripropylene glycol diacrylate	≤8	~18 000	• high reactivity and hardness • excellent adhesion on various substrates • high gloss • good corrosion resistance
GENOMER* 2255	Rahn AG	modified BPA epoxy diacrylate	≤3	~45 000	• very good pigment wetting • medium up to high reactivity • high gloss • good hardness and scratch resistance • good abrasion and solvent resistance
GENOMER* 3364	Rahn AG	modified polyetherpolyol acrylate	0.5	~130	• high reactivity, hardness and scratch resistance • high gloss • good flexibility • good abrasion and solvent resistance • low yellowing
GENOMER* 3457	Rahn AG	polyether acrylate	0.2	~1250	• excellent reactivity, hardness and scratch resistance • very good solvent resistance • outstanding adhesion to a variety of substrates
GENOMER* 4590/PP	Rahn AG	aliphatic urethane acrylate in 25% PPTTA	1	~11 000	• high reactivity hardness and scratch resistance • high abrasion resistance • solvent and stain resistance • low yellowing
PHOTOMER® 5429	IGM Resins	tetra functional polyester acrylate	N/A	150÷500	• good adhesion to metal substrates • excellent pigment wetting, flow and leveling
PHOTOMER® 6210	IGM Resins	aliphatic urethane acrylate	N/A	8500÷15 000	• non-yellowing • excellent light stability • good chemical and abrasion resistance • high flexibility

Source: own study based on [27–29].
Źródło: opracowanie własne na podstawie [27–29].

Table 5. Examples of commercially available adhesion promoters dedicated to light-curing varnishes applied on metal substrates
Tabela 5. Przykłady dostępnych w sprzedaży komercyjnej promotorów adhezji przeznaczonych do lakierów światłoutwardzalnych nanoszonych na podłoża metalowe

Product	Distributor	Chemical character	Acid number [mg KOH/g]	Viscosity at 25°C [mPa · s]	Usage level [wt% on total formulation]
EBECRYL® 168	Allnex	acidic methacrylate	250÷330	900÷1900	1÷5
EBECRYL® 170	Allnex	acid modified acrylate	270÷330	~3000	1÷10
EBECRYL® 171	Allnex	acidic methacrylate	250÷330	850÷1850	1÷5
GENORAD* 40	Rahn AG	methacrylated phosphate ester	295	~2000	1÷5
GENORAD* 41	Rahn AG	methacrylated phosphate ester	290	~1500	1÷5
PHOTOMER® 5028	IGM Resins	chlorinated polyester in 40% GPTA	25	~95 000	N/A
PHOTOMER® 5041	IGM Resins	chlorinated polyester in 40% TMPTA	25	~95 000	N/A

Source: own study based on [27–29].
Źródło: opracowanie własne na podstawie [27–29].

oxide (BAPO), 2-hydroxy-2-methylpropiophenone (DMHA), methyl benzoylformate (MBF), diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) and ethyl(2,4,6-trimethylbenzoyl) phenylphosphinate (TPO-L). To obtain UV-curable recipes of high quality in both liquid and cross-linked forms, auxiliary agents with anti-foaming, defoaming, leveling, wetting, dispersing or anti-cratering properties are also used. However, because of shrinkage occurring during photopolymerization, the agents that improve adhesion to metal are the most important from the perspective of coatings formulations for metal substrates. It is assumed that the adhesion of UV coatings applied to a metal substrate is influenced by two key factors: the use of a flexible polymer matrix based on low-functional acrylates (it has a lower cross-linking density but shows lower shrinkage during photopolymerization) and the above-mentioned addition of acidic adhesion promoters to the composition (acrylate or methacrylate functional derivatives of phosphoric acid, which improve the adhesion of the coating to the substrate, but can initiate corrosion processes and are incompatible with its inhibitors).

The base of raw materials for obtaining light-curing solutions is constantly growing, and companies are offering new products dedicated to coatings on metal substrates. The chosen materials currently available for commercial sale in Europe are presented in

Tables 4 and 5. In addition to the raw materials for the production of UV coatings, ready-made coating solutions developed by R&D departments of research institutes and industrial centers are also available for sale. The range of available varnish products is wide and depends on the base material, it includes varnishes and varnish primers sold by Polish and foreign companies, such as: PPG Industries, C.H. Erbslöh, Remmers, Finixa, Pallmann or Kedar. Despite the difficulties associated with the limited adhesion of UV coatings to metal and problems with providing protection against corrosion, such industrial solutions exist. Both varnishes and UV--cured powder coatings are used in the automotive industry and for painting machine parts or pipes.

6. Summary and perspectives

Reflections on modern coating solutions for the protection of metal substrates appear not only in numerous scientific works devoted to this subject, but also in emerging patent applications and new products available for commercial sale. A strong pro-ecological trend is observed, which assumes giving up varnish products based on organic solvents, and replacing them with water-based or 100% solid products. Thus, in the protection against corrosion, it is proposed to use, for example, epoxy paints with a reduced content of zinc dust [30], coatings based on conductive polymers [31], with carbon nanoadditives [32], applying ceramic coatings [33] and even using plants extracts as corrosion inhibitors [34]. Due to a number of green attributes, the formulation of UV-cured paints and varnishes perfectly fits the above assumptions.

This article proves the legitimacy of this claim by presenting the theory and the latest scientific achievements in this field in a short and accessible way. A review of the raw materials used for the preparation of UV formulas was made. The oligomers, diluents/monomers and photoinitiators used, together with the mechanisms of photopolymerization of the finished coatings, were described. Importantly, UV raw materials that are offered for sale by key manufacturers of the chemical industry both in Europe and worldwide have been collected and included in the tables. Based on the data presented in the above review, it can be said with great certainty that due to the environmentally friendly profile and a number of advantages related to e.g. reduction of energy and costs of the technology of UV protective coatings, this field will flourish in the coming years.

It is worth remembering, however, that currently the majority of UV raw materials used on an industrial scale are still of petrochemical origin. It is not known for how long, and if ever, it will be possible to fully replace such materials with materials derived at least partially from renewable sources (currently only some oligomers and reactive diluents). Attempts to synthesize new, improved oligomers and photoinitiators (including those with low-migration potential) by scientists from the industry and academics both, will contribute to the creation of increasingly perfect varnish products and coatings. These, in turn, will gradually displace current solutions, to the benefit of us, users, and above all, for our planet.

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