

Tracking down the Causes

Phenomenon of Reversible Discoloration of Plastic Components Explained (Part 1)

A previously unexplained phenomenon occurring in interior and exterior automotive components has long troubled auto manufacturers and suppliers: light-colored components discolor when stored for any length of time in the dark. But then in the daylight, this discoloration disappears again within a couple of days. Extensive tests and special analysis have now solved this mystery.

The automotive industry is increasingly moving towards individual, demand-led production and supply of its vehicles. This poses enormous challenges with regard to the logistics and quality of supplied parts. Suppliers have to deliver their components just-in-time to the auto manufacturers. To avoid delays, suppliers frequently hold quite large stocks, as a result of which the components are often stored covered up in the dark for weeks.

Plastic components stored like this, especially those with light-colored surfaces (painted or unpainted), have for years exhibited an unexplained phenomenon, i.e. in some cases, they discolor in the dark. Exposure to daylight for a couple of days reverses this discoloration. The effect is increased in winter when the sun's rays are weaker and condensation forms on the components during cold nights. The color difference is particularly marked when only a covered area of the component discolors. With darker shades, this discoloration is less visible for optical reasons.

If plastic components that have become discolored after storage in the dark are installed directly next to freshly produced components in the vehicle, a color difference shows up that fails to meet the relevant quality standards of the auto manufacturer. For this reason, non-compliant components are separated out during assembly. It is only possible to use these discolored components and make them compliant with the standards by expending considerable time and money on exposing the components to light, sorting, scrapping, or post-finishing them. The costs so incurred are always a con-



Automobile C pillar laminated to thermoforming film: in the dark, the component underwent pink discoloration (front right). On exposure to light, the discoloration was reversed (original, back left) (© Daimler)

tentious issue because it is not possible to determine precisely the originator of the fault or define an immediate measure to rectify it.

Searching for the Causes

In a major joint project (see **information box**) led by Daimler AG, Sindelfingen, Germany, the causes of reversible discoloration were sought. The aim was to find the reason for dark time discoloration, develop a test to investigate the problem, and devise suitable ways to prevent reversible discoloration of plastic components.

The initial approaches concentrated on reversible discoloration of vehicle interior components. The phenomenon affects very many components in vehicle

interiors, e.g. C pillars (**Title figure**), doors, instrument panels, roof linings, and head restraints. Plastic components in car interiors are subject to high quality requirements in terms of odor, color, and robustness. Various materials are used here, such as thermoplastic polyolefin (TPO) or polyvinyl chloride (PVC) films, synthetic leather made from PVC or polyurethane (PU), and natural leather. These different materials must harmonize with each other. What they all share in common is a painted surface. The investigations were therefore confined initially to discolored paints, because in all cases it was only the paint on the surface that was discolored. Any influence by the substrate was ignored at first. Different unpainted plastics were also studied. In the visual assess- »

Fig. 1. Discoloration resulting from the reaction of phenolic antioxidants with nitrogen oxides to form a nitrophenolic compound (© BASF)

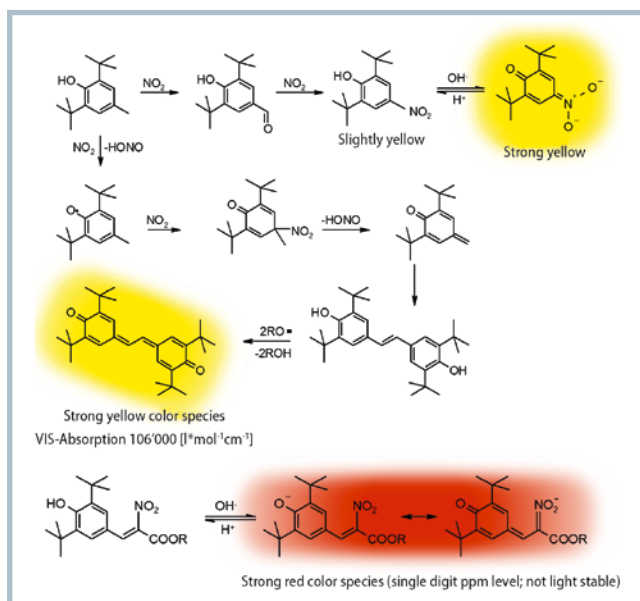
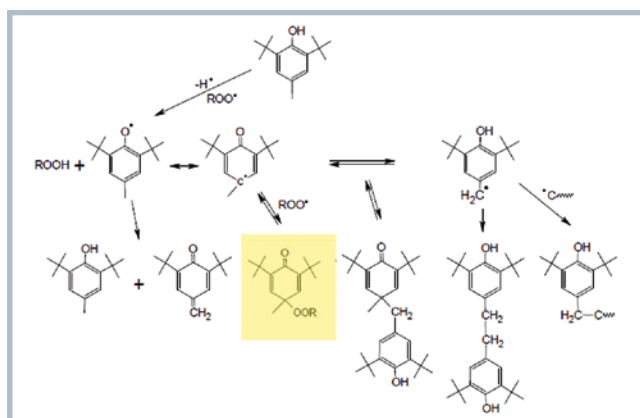


Fig. 2. Known mechanisms for the mode of action of antioxidants: the colored quinone form (marked yellow) leads to discoloration of paints and plastics (© BASF)



ment of the discolored paints and plastics, a spectrum of different shades was observed, ranging from very pale lemon yellow through orange to deep pink. When the surface was exposed to light, the discoloration disappeared again. A scientifically convincing explanation for the different discolorations was not found despite numerous tests and different attempts to explain.

Known and Assumed Effects

The project participants used previously known mechanisms for the discoloration of polymers as their starting point. Only the main ones are considered in this article.

Normal oxidative, thermal or light aging of polymers: Through aging, degradation of the polymer takes place. The discoloration so caused is dirty yellow and non-reversible [1, 2]. Resistance is tested by heat storage and/or light aging.

With a certain amount of analysis, degradation of the polymer can be detected. For example, after oxidative heat/light aging of PU foam – alongside the formation of different organic acids, aldehydes, and alcohols – degradation of the isocyanate groups in the aromatic polyurethane can be identified. The compounds so formed, which contain an azo group $-\text{N}=\text{N}-$ and the nitro group $-\text{NO}_2$, color the foam yellow to brown.

Effect of amines on solvent-based paints: In the past, amines from adjacent PU foams frequently caused discoloration of solvent-based paints. The discoloration is dirty yellow or brown and non-reversible. It is attributed to the effect of a special PVC that used to be added to solvent-based paints on PVC film and synthetic leather for cost and technical reasons (better HF weldability, e.g. for sun vizors). This PVC component in the paint either had a different stabilizer or was not stabilized at all and consequent-

ly entered into a decomposition reaction with amines [3]. It is generally assumed that amines promote thermal cleavage of the hydrochloric acid in the PVC polymer by formation of ammonium chloride salts and so decompose the PVC polymer (the VDA 230-223 test of January 2014 applies to some material specifications). Over the last ten years, however, aqueous paints have replaced solvent-based ones. With aqueous paints, the PVC filler can only be incorporated into those that are acrylic-based. Today, however, PU-based paints are predominantly used. Hence this type of yellowing only rarely occurs now on adequately covered painted PVC surfaces.

Effect of amines during storage in contact with foam: Painted PVC surfaces are discolored by amines during storage in contact with foam (e.g. VW Indicator Film Test Method PV3937 or Ford JSN 30.60.08). Certain components in the PVC possibly react with amines to form a colored compound [3]. However, the precise mechanism is not known. Perhaps it is a case here, too, of a "dark time yellowing" or "dark time pinking" reaction initiated by a change in the pH value.

Contact reaction in flame lamination: Pyrolysis products resulting from quite intensive flame lamination of painted decorative material to PU foam can lead to irreversible discoloration through contact of the back with the paint surface. Since the usual aromatic-based PU foams are not light-stable, the pyrolysis products deposited on the paint oxidize in the presence of light and/or oxygen. The fragments from the PU foam pyrolysis can be relatively easily detected by Fourier transformation infrared (FTIR) spectroscopy, since PU paints are usually aliphatic-based. Discoloration by other components (e.g. flame retardants or adhesives) is also relatively easy to detect analytically.

Reactions of nitrogen oxides with phenolic antioxidants: A discoloration not yet clearly explained can be caused by nitrogen oxides (NO_x). Diesel-powered forklift trucks are often cited as the source of increased nitrogen oxide concentrations in the confined space of a warehouse. There are numerous publications and test methods which assume that this discoloration is caused by a chemical reaction of nitrogen oxides with phenolic antioxidants in the paint (e.g. tests as per

VDA 230-222 of August 2013 and AATCC 164) [4]. The end product – according to the assumption – consists of a nitrophenolic compound (**Fig. 1**) [4]. Cleavage of the nitro group is not readily possible. This means that the classic discoloration due to the formation of nitrophenols is irreversible.

The relevant test methods are based on the addition of NO_x to or in-situ creation of NO_x in a test sample within a closed vessel, e.g. an excicator. The differences between the test methods lie only in, for example, the different NO_x quantities, test temperatures, and test times. In these tests, the NO_x concentrations far exceed any usual or real emission. In some cases, the discoloration can only be produced with an NO_x content that exceeds the maximum actually measured air values on busy streets by a factor of 10^6 .

Reactions by phenolic constituents: Discoloration of paints and plastics could also be attributed to phenolic constituents on the material surface. Here the experts often only cite the usual general mechanisms for the mode of action of antioxidants (**Fig. 2**) [2].

Discoloration by phenols in textiles and shoes that are transported long distances, e.g. from Asia to Europe, is known. A test has been developed for this (DIN EN ISO 105-X18), which is intended to show the potential of textiles to be discolored by phenols. A test paper treated with about a 0.1% solution of 2,6-di-tert-butyl-4-nitrophenol is stored for 16 hours in

contact with the textile sample at elevated temperature (50°C) under a 5 kg weight. At the same time a control fabric is also tested. The discoloration reaction is reversible. The discoloration in this test is similar to the dark time discoloration of paints and plastics.

These previously known effects and tests relating to the discoloration of plastics and paints could be helpful in finding the causes of reversible dark time discoloration of materials. By gaining an understanding of the mechanisms involved, measures can then be developed to rectify the problem.

Measurement and Detection

Explaining the reversible discoloration of plastics and paints after prolonged storage in the dark required a considerable amount of analytical work. In the studies, the samples discolored in the dark gave no hint of any NO_x - and amine or other known effect. For this reason, those involved in the project suspected an oxidation reaction and selected appropriate test methods.

X-ray photoelectron spectroscopy (XPS): With the XPS test method, it was possible to detect an increase in ketone/aldehyde groups in a sample of the discolored paint (**Table 1**). The reaction was reversible. After exposure to light, the previous status quo for the C-O groups was for the most part restored. In other words, this oxidation was only temporary. »

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Series

Part 2 of the series on the reversible discoloration of plastics in auto manufacture describes further studies on "dark time discoloration". This article will appear in the August issue of *Kunststoffe international*.

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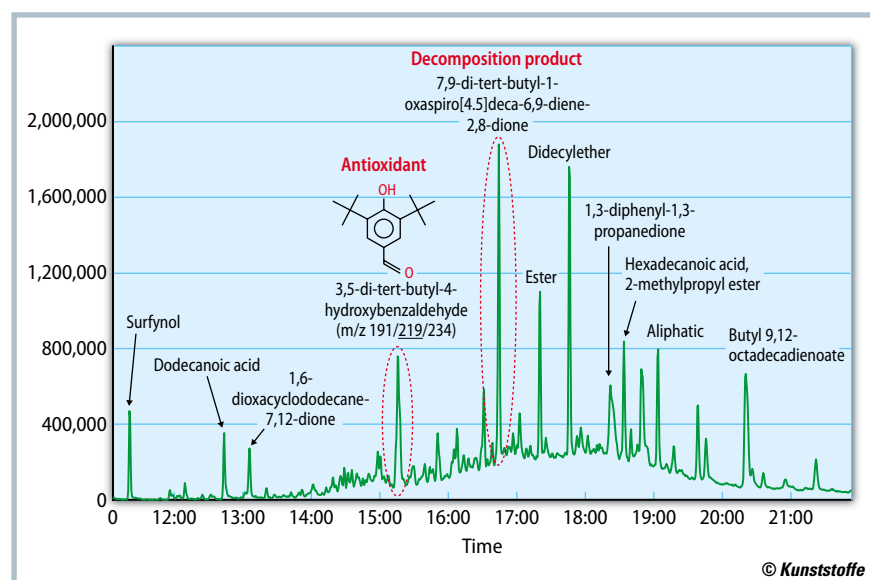


Fig. 3. Emission analysis of a discolored paint: detection of organic acids and antioxidant degradation products (Quelle: Daimler)

Fig. 4. Metals catalyze the discoloration: selective discoloration of paints due to metal agglomeration after aging in artificial light at high temperature (discolored areas left and right were covered with a metal sheet)

(© Daimler)



X-ray fluorescence analysis (XFA):

Measurements with a special instrument from Jeol (Germany) GmbH, Freising, Germany, led to a highly promising explanation for the causes of dark time discoloration. In all the paints with a tendency to discoloration, it was possible to detect metals, e.g. silver or iron. The usual XFA instruments were not able to detect this.

Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopy: Very refined FTIR and NMR analysis showed that the paints and plastics with a tendency to dark time discoloration usually contained several light stabilizers and/or antioxidants.

Secondary ion mass spectrometry (ToF-SIMS): The ToF-SIMS study repeatedly detected an organic compound that could not be clearly identified. This could be attributed to a colored quinone or ketone form of the antioxidant or light stabilizer (see also part 2 of this article to appear in the August edition). Absolute detection was not possible because the compound was unstable and was not available as a reference substance for analytical tests.

Thermodesorption analysis of organic emissions (VDA278): Emission measurements carried out according to VDA278 revealed significant amounts of organic acids in the discolored samples. Antioxidant degradation products were

also detected (Fig. 3). Apparently, an oxidation reaction had also taken place.

Deducing the Mechanism

In the tests described above, the additives contained in plastics and paints, such as antioxidants, light stabilizers, and metals, were particularly identified as initiators of reversible discoloration. Specific mechanisms take place, depending on the product, and this allowed the project participants to deduce a complex mechanism for dark time discoloration.

Antioxidants in paint or plastic discolored under the effect of heat and darkness when in external contact with a metal surface. In this case, phenolic-based products convert temporarily to the colored quinone form. The polymer matrix stabilizes this form. The amount of antioxidant plays a role here. If the optimum addition required to protect paint or plastic is significantly exceeded, the excess antioxidant reacts to produce dark time discoloration.

Light stabilizers in paint or plastic change color if a component is stored for a prolonged period in the dark after activation by light and external contact with a metal surface. Products, e.g. based on benzotriazoles, convert temporarily from the enol form to the colored ketone form. Here, too, the polymer stabilizes the col-

ored form. Once again, the amount of light stabilizer has an influence: if significantly more additive is used than required, then dark time discoloration takes place. In practice, this effect occurs particularly with light-colored plastics and paints on light-colored surfaces.

Metals (e.g. silver and iron) in paint or plastic act as catalysts for discoloration. Contamination of plastics or paints with silver can happen deliberately or accidentally. Many aqueous titanium dioxide (TiO₂) suspensions or powders contain silver additives or are contaminated with silver. The same applies to silicate or silicone additives. Silver is sometimes added to the water of aqueous paint solutions as an effective antimicrobial agent. Even when silver content had not been declared, traces of silver were detected in very many paints. Nanosilver tends to agglomerate in dispersions, which would explain selective discoloration (Fig. 4). It is also likely that abraded iron particles are present in every manufacturing process.

Explaining Discoloration

The discoloration was reproduced by exposing a relatively freshly painted sample containing several light stabilizers and antioxidants as well as silver contamination to light (aging in artificial light at high temperature, DIN EN ISO 105-B06 or solar simulation, VDA 230-219). In this test, part of the sample was covered with an iron sheet. The area covered by the metal sheet was discolored (Fig. 5, top area of the sample). When, in the same light exposure test, a thin sheet of glass was placed between the sample and the metal sheet (preventing any contact between the sample and the metal), no discoloration was observed in the dark areas. When there was direct contact between the sample and metal in only part of the covered area, the entire covered area was discolored. The discoloration was somewhat weaker for the same test duration. With samples more than two years' old, dark time discoloration is very unlikely.

The following conclusions could be drawn from the tests: If the plastic surface contained light stabilizers and antioxidants along with metal constituents (e.g. silver and iron), the discoloration reaction started when the sample came into further external contact with metal (e.g. thermoforming mold or metal mount-

Sample	C1 [at %]	C2 [at %]	C3 [at %]	C4 [at %]	C total [at %]
1 discolored	72	18	7	4	65.8
2 not discolored	85	3	9	3	67.5
3 sample with discoloration reversed after exposure to light	84	4	9	3	68

Table 1. Paint analysis of three different samples with XPS: C content of the top 5 to 10 nm of the analyzed surfaces (source: Daimler)

ing). When the sample was then stored in the dark, the reaction continued. The discoloration spread autocatalytically. We know that metals are responsible for this from the degradation mechanism of plastics [1]. Moisture ((condensation in winter) and pH also had an indirect influence on discoloration. The discoloration was reversible.

On further testing of areas where dark time discoloration had been reversed by exposure to light – as described above – a weaker discoloration was observed but only if the testing cycle “dark phase/light phase/renewed dark phase” was conducted over a short period of time (within days). The longer the time was between the first and subsequent discoloration phase, the lower the possibility of renewed discoloration.

The color resulting from the discoloration reaction was usually mixed, depending on the type and amount of light stabilizer and antioxidant used. Phenolic additives tended to exhibit yellow discoloration, while nitrogen-containing or aminic additives gave rise to pink shades. It was also found that effective light stabilizers or antioxidants have a greater tendency to dark time discoloration when used in excess.

Conclusion and Solutions

Paints and plastics normally contain both antioxidants and light stabilizers. In conjunction with environmental influences, these additives can cause dark time discoloration if they are present in the materials to excess. Metal constituents catalyze the effect. Moisture and pH may also have an influence.

As the studies conducted verify, a temporary apparent oxidation reaction takes place. The radicals of the two additives thus formed can be “preserved” in the polymer in a relatively stable form. This form is colored. Phenolic antioxidants usually have a pale to intense yellow color in the radical-stabilized form. Aminic antioxidants and light stabilizers exhibit pink or red shades. If the discolored components are exposed to light for a certain period of time, the structures formed in the dark are reversed. In other words, the components regain their original shade.

This discoloration can be reproduced by partially covering the plastic surface (painted or unpainted) with a metal sheet (e.g. iron or aluminum) in the usual tests for climate, heat, and/or light aging. If the paint or plastic has been contaminated with redox-active metals, the surface discolors.

Additives such as phenolic or aminic antioxidants and light stabilizers are indispensable both in the actual process of manufacturing e.g. plastics, paints, adhesives, and raw materials and for the long-term stability of these products. To prevent these undesirable discoloration reactions, the only solution is to reduce the amount of additives used to the absolute minimum necessary or develop alternative antioxidants. Complete control of the amount and type of antioxidants used in the serial production of e.g. plastics, films, natural leather, and synthetic leather – particularly when they are produced at different global sites – is hardly possible to achieve. Exclusion of moisture is also impossible in reality.



Fig. 5. Reproduction of discoloration: testing a painted surface containing several light stabilizers and antioxidants as well as silver contamination after solar simulation in accordance with VDA 230-219; the top area of the sample was covered with a metal sheet (above) (© Daimler)

Metal contaminants (e.g. silver and iron) in paints and plastics catalyze discoloration reactions such as dark time yellowing and dark time pinking in the presence of the above-mentioned additives. It is likewise not possible to guarantee that materials are absolutely free of metals. The only solution at present is to chemically bind the metal content. For this purpose, the plastics industry uses e.g. the additive Irganox MD1024 from BASF. For paints and foams, a new additive must be developed and tested. ■