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Abstract

This paper discusses phosphorescent or 'glow in the dark' paint and its problems, characteristics and treatment possibilities, while using an artwork without title (1968, RMT, Enschede) by IMI Giese as case study. To understand the problems that can occur with this little examined material, it is crucial to know how phosphorescence works and what the composition and properties of different phosphorescent pigments are.

The conservation challenges for this specific artwork are mostly due to the properties and composition of the paint: the lacunas for instance are a direct effect of the stickiness of the paint layer. The challenging search began for a phosphorescent retouching paint with an identical daylight colour and an afterglow with a similar colour, intensity, and duration as the original Wiedolux paint. Since all readily available phosphorescent paints and pigments did not match the properties of the original paint layer, it was necessary to manipulate self-made phosphorescent paints. The ways of manipulation have been tested through visual and technical analysis. This study provides insight into the results of the test sequences and offers useful information about the way conservators can adjust the properties of a phosphorescent retouching material to suit their needs.

Keywords: phosphorescence, retouching, IMI Giese, zinc sulphide. ZnS:Cd

1. Introduction

In the 1960s, phosphorescent paint became a hype when it was commercially introduced as an artist material. The magical properties of the material were exploited by many artists of the time. One of these artists was the German minimalist Rainer 'IMI' Giese, who was impressed with the spaciousness the paint created in the dark. An artwork without title (1968) from the sub-collection Depot VB/VR of the Rijksmuseum Twenthe in Enschede (Holland) is part of his phosphorescent series *Leuchtwerke* [Fig. 1, 2].[1] This artwork is damaged and requires treatment. The conservation challenges herein lie mainly in the properties and composition of the paint used in the work. To understand the problems that can occur with this interesting, yet little researched material, it is important to know how phosphorescence works and what the composition and properties of the different phosphorescent pigments are.

Figure 1. The case study without a title by IMI Giese (1968, Rijksmuseum Twenthe, Enschede, the Netherlands) in daylight

1.1 Phosphorescence

Phosphorescence can be found all around us: on the dials of our watches, the security exits and the glow-in-the-dark stars on the ceiling of a child's bedroom. Phosphorescent objects have an enchanting effect: when the light goes off, they produce an afterglow until they eventually fade out. This process can last minutes or even hours. But what happens exactly? What are the properties of a material with an afterglow?

Many organic and inorganic materials are luminescent, which means that they produce visible or invisible light after they have been exposed to energy. There are eight different kinds of luminescence, one of which, photoluminescence, is key to this subject. The process of luminescence is different from regular colour perception. The latter is mainly focused on the absorption and *reflection* of light, whereas in photoluminescence, a material will absorb electromagnetic radiation that will result in the emission of visible or invisible light. For this emission to occur it is essential that the photoluminescent material is exposed to light of a minimum frequency (energy) first, which is dependent on the composition of the raw material. The characteristic colour of the emitted light always has a lower frequency (colours more towards the red than the blue) than the frequency that was

[1] Inventory number 4851 (1) + (2)

absorbed.[2]

There are two different kinds of photoluminescence, namely fluorescence and phosphorescence. Even though there is a significant difference between the two, in practice these terms are often interchanged. When photoluminescent pigments emit light within a fraction of a second, we speak of fluorescence.[3] Because this process happens within a very short period of time, the material will not produce an afterglow. When the source of energy is taken away, the photoluminescent effect of fluorescent material will not be visible. Phosphorescent materials, however, can retain energy after absorption and will produce an afterglow whilst slowly releasing this energy. The composition of the material will determine the duration of the afterglow.[4]

1.2 Phosphorescent pigments

There are multiple materials that have phosphorescent qualities, and not all of them are suitable to use as a phosphorescent pigment. Although the phenomenon of phosphorescence has been recognized for some time, the development of a stable phosphorescent pigment proved to be difficult and even now industry is still improving the properties. The pigments that are most often applied are zinc sulfide pigments and rare earth pigments. Both phosphorescent materials have their own specific composition and characteristics.

1.2.1 Zinc sulfide

Zinc sulfide (ZnS) was the first phosphorescent pigment produced on a large scale since the beginning of the twentieth century. It is an inorganic compound of zinc and sulfide, in the form of an opaque, white/yellow powder. Zinc sulfide itself is not phosphorescent, although a surplus of zinc or sulfide does give the material certain phosphorescent properties. The *dopants* in the pigment are crucial in obtaining an afterglow.[5] A dopant is an impurity in the crystal matrix of a host material, which ensures that the energy will be absorbed effectively. Also, a dopant can have an influence on the absorption and emission spectrum of pigments. These impurities often consist of [transition] metals like copper, aluminum, cadmium, manganese and silver. They can also be halogens, like chlorine.[6] The first dopants were usually small phases of copper in the crystal structure, resulting in the pigment ZnS:Cu.

To bring about the best possible phosphorescence, the raw material needs to be very pure and the dopant should be carefully added in dosed quantities.[7] The dopant and the concentration of the dopant have a crucial influence on the emission spectrum and the effectivity of the afterglow of the pigment. The optimal phosphorescence of zinc sulfide pigments is dependent on the exposure time.

[2] Ashdown, I., 'Glow and Behold', *Industry News*, 25 March 1999, p.2

[3] There are some exceptions to this rule. The most important differences between fluorescence and phosphorescence take place at micro level.

[4] Martindill, M.G., 'A European Eye on Luminescence: Fluorescent and Phosphorescent Colours for the Visual Artist', *Leonardo*, Vol. 21, No. 2, p. 187

[5] Strange, J.W., 'The Chemical and Physical Properties of Luminescent Materials', *paper read to the Colour Group*, 11 December 1942, p.368

[6] http://glowinc.com/glow-in-the-dark/glow-in-the-dark-technologies.aspx (consulted October 2014)

[7] Mirhabibi, A.R., M. Rabiee, R. Aghababazadeh, F. Moztarzadeh en S. Hesaraki 'Preparation of and Photo- and Electroluminescence Characteristics of ZnS:Cu fosfor', *Pigment and Resin Technology*, Vol. 32, Iss.6, 2003, p.358

When the material is exposed to visible light for a minimum of five minutes, the pigment is completely 'activated'.[8] Also, ZnS:x pigments (zinc sulfide pigments doped with an unknown metal) are more effective when they absorb energy from deep blue to ultraviolet light.[9] Even for optimal mixtures, the zinc sulfide pigments are not very bright and have a short afterglow. These properties might seem undesirable, but ZnS:x is often still added to commercial glow-in-the-dark paint, plastics etc. because it is relatively cheap .[10]

1.2.2 Rare earth pigments

Rare earth pigments are inorganic, hard, opaque, phosphorescent pigments with a long afterglow. The base materials of the pigments are elements like strontium, magnesium, calcium, barium, silicium and titanium in an oxide crystal matrix to which rare-earth dopants are added. The raw material is easily mixable with other elements and it is chemically more stable than ZnS:x.[11] The rare earth pigment that is used most often in the industry is strontium aluminate (SrO-Al2O3). Of the possible dopants, the rare earth metal europium is most widely used.

Just like ZnS:x, the duration of the phosphorescence of rare earth aluminates is dependent on the exposure time. The rare earth aluminates have an excitation time of 30 minutes to become fully activated. This is six times longer than ZnS:x. but the afterglow of rare earth aluminates is fifteen times as bright as that of ZnS:x.[12] The emission spectrum of rare earth aluminates can vary from green/yellow to a purplish blue.[13]

1.3 Phosphorescent paints in art

In the 1950s and 1960s, artists from different art movements became interested in this 'new' material. Previously, phosphorescent pigments and paints were only available to a select group, like the army and industry. The popularity of the phosphorescent artist materials was mostly due to the 'newness' of the material, but the afterglow of the effect paint undoubtedly also triggered associations with popular contemporary themes like the Russian and American fixation on space travel, science fiction and the moon landing in 1969. This fascination for glow-in-the-dark materials hasn't dissipated, and contemporary artist still utilize them. Famous artists that have used phosphorescent paint in their art, are Lucio Fontana, Konrad Lueg, Piero Manzoni, Gilberto Zorio, Chris Ofili and Antony Gormley, to name a few.

Among all the artists found during the inventory, only one has used the material systematically in his oeuvre, namely Rainer 'IMI' Giese (Neheim-Husten, 1942-1974). IMI Giese was a German minimalistic artist. A part of his career is inextricably tied to the work of his colleague Klaus Wolf Knoebel (or 'IMI' Knoebel), whom he met during his studies at the Werkkunstschule in Darmstadt. In 1964 they formed the joint identity IMI (ich mit ihm, or I with him), however, despite this, they usually made their own artworks.[14]

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[8] *About Photoluminescence. A Brief Technical Introduction*, Baring Technologies P/L, 2011, p. 6
[9] Ashdown, I., 'Glow and Behold', *Industry News*, 25 March 1999, p.3
[10] http://glowinc.com/glow-in-the-dark/glow-in-the-dark-technologies.aspx (consulted October 2014)
[11] Panigrahi, B.S., 'Long Afterglow Phosphors', *Science 53*, p.106 via website van de Indira Gandhi Centre for Atomic Research: www.igcar.ernet.in/benchmark/science/53-sci.pdf (consulted October 2014)
[12] *About Photoluminescence. A Brief Technical Introduction*, Baring Technologies P/L, 2011, p. 6
[13] http://glowinc.com/glow-in-the-dark/glow-in-the-dark-technologies.aspx (consulted October 2014)
[14] Weibel, P. (ed.), *IMI Giese*, exhibition catalogue Kunstverein München, Kunsthalle Zürich, Neue Galerie am Landesmuseum Joanneum Graz, Ostfildern, 1994, p.42

The use of phosphorescent paint in the artworks of IMI Giese is prevalent in his 2D and 3D works. The afterglow is used to create an extreme geometric spaciousness in a dark environment. In the catalogue of the solo exhibition *Rainer Giese. Ausgewahlte Arbeiten* that was organized four years after his death, photos of a small overview of his phosphorescent works were published. They consisted mostly of painted beams, frames, angles, blocks and plates of wood or fiberboard in different dimensions and arrangements.

1.4 Case study: without title by Rainer 'IMI' Giese (1967)

The case study that forms the basis of this investigation was made during Giese's sculptural period in which he wanted to emphasize spaciousness by applying a phosphorescent paint. The artwork consists of two timber pieces of the same length (110 x 4,7 x 4,7 cm). The phosphorescent paint is applied on a white ground. The paint layer looks yellow in daylight and has a green-yellow afterglow in the dark. On both beams, at about 20 cm from the far end, the word 'IMI' is written on the paint with a crayon (possibly Wasco). During exhibition, the two timber pieces are balanced against the wall, a few centimetres apart from each other. Figure 2 gives a good impression of how the artwork should be installed and its impact in a dark space.

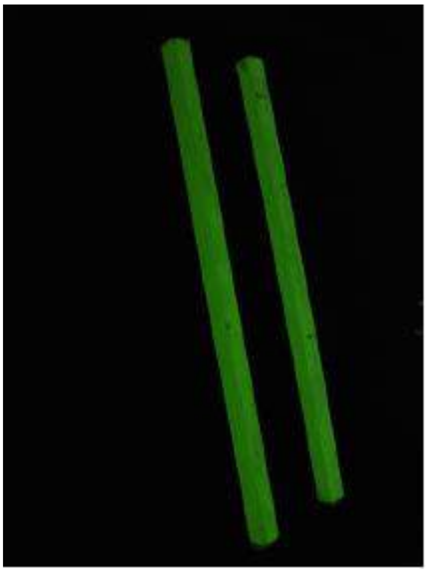

Figure 2. The case study in the dark, positioned as it ought to be exhibited.

In the aforementioned exhibition catalogue from 1978, it is mentioned that Giese made use of a phosphorescent paint with the brandname *Wiedolux*. Unfortunately, this brand of paint is not in production anymore and there is no archival information available about the product. Because of this, it was necessary to carry out technical analyses to find out more about the composition of the layers. This was executed by the Cultural Heritage Agency of The Netherlands (RCE) and led by Katrien Keune. A combination of FTIR and SEM/EDX analysis indicated that the white ground consists of an acrylic, mixed with fine, tightly packed pigments. The elements titanium and barium are prevalent, which is most likely due to the presence of the inexpensive white filling materials titanium dioxide and barium sulfate. The composition of the paint layer was determined with the same analytical methods. The paint is an acrylic (most likely the same binder as the ground) with phosphorescent zinc sulfide pigments that are doped with cadmium. Complementary research at the CICRP in Marseille, done by Alain Colombini, confirmed these findings and concluded that the binder of ground and paint is supposedly a poly methyl methacrylate (PMMA).

1.5 Properties of the material, consequences and challenges

The binding material of the ground and the paint is an acrylic and the properties of this material are the most important reason for the majority of the damages. The soft paint layers with the consistency of chewing gum make the artwork sensitive to mechanical damage and the attraction – and enclosure – of dirt. When looking at the condition of the artwork, it is possible to see that the material causes problems. The lacunas in the paint layer are a direct effect of the stickiness and are the biggest conservation challenge. It appears that the beams have been in contact with each other for a long time, which presumably is the reason why they have adhered to each other. In an attempt to separate them, a paint transfer took place, where the paint layers of one piece of timber transferred onto the other exposing the wooden substrate. As no phosphorescent paint remains in these areas, they present as black spots when exhibited in the dark. The biggest lacunas can be re-filled with original material that is transferred back, but in some cases this is not possible. Suitable retouching pigments and medium had to be found.

From the start, the search for a suitable retouching medium proved to be challenging. Due to health and safety regulations, cadmium can no longer be used for the production of phosphorescent pigments. This means that the materials available on the market today have different properties than the material that Giese used.[15] The addition of a cadmium dopant has a positive influence on the intensity and duration of the afterglow: they are higher than that of the (mostly copper-doped) zinc sulphides which are widely available today, but not as high as that of the rare earth pigments. The presence of cadmium also changes the emission spectrum of the phosphorescent material by shifting it slightly from the green to the red range. These effects prove to be difficult to imitate with the phosphorescent pigments available today. To achieve the desired result, it was necessary to modify the available materials.

2. Methodology

2.1 Selecting test materials

A suitable retouching medium needs to have similar colour as the original in daylight, but should also have a comparable colour, intensity, and duration of the afterglow in the dark. To find out how it would be possible to manipulate the available pigments, tips and tricks from industry were catalogued and applied. In this case, it would be necessary to intensify the phosphorescence of zinc sulfide pigments, or the strontium aluminates needed manipulation in order to decrease their effectivity. Also, more information needed to be gained about how to manipulate the colours of the paint in daylight and in the dark. Aside from this manipulation, suitable phosphorescent pigments and a binder had to be chosen.

2.1.1 Selecting ways of manipulation

By comparing the information available in industry and the needs of the conservator, eleven different ways of manipulation have been chosen [Table 1].

[15] Keune, P., 'Fosforescerende Verven', *kM* 0, autumn 1991, p.24

Nr.	Recipe and way of manipulation
1.	33,3% phosphorescent pigment, 66,6% Plextol B500 The phosphorescent pigment is washed for two hours in demineralised water before mixing it with the medium
2.	33,3% phosphorescent pigment, 66,6% Plextol B500 The phosphorescent paint is applied on a black surface
3.	33,3% phosphorescent pigment, 66,6% Plextol B500 The phosphorescent paint is applied on a white surface
4.	25% phosphorescent pigments, 55% Plextol B500, 20% glass microballoons, Glass microballoons are added as a filler
5.	25% phosphorescent pigments, 55% Plextol B500, 20% Aerosil Aerosil is added as a filler
6.	25% phosphorescent pigments, 55% Plextol B500, 20% calcium carbonate Calcium carbonate is added as a filler
7.	33,3% phosphorescent pigment, 66,6% Plextol B500 The phosphorescent pigment is grinded before mixing it with the medium
8.	40% phosphorescent pigment, 55% Plextol B500, 5% cadmium yellow light Cadmium yellow light is added as a regular pigment
9.	40% phosphorescent pigment, 55% Plextol B500, 5% nickel titanium yellow Nickel titanium yellow is added as a regular pigment
10.	25% phosphorescent pigments, 55% Plextol B500, 20% aluminium hydroxide Aluminium hydroxide is added as a filler
11.	25% phosphorescent pigments, 55% Plextol B500, 20% titanium dioxide Titanium dioxide is added as a filler

Table 1. Overview of the recipes and different ways of manipulation of the 11 different self-made paints

2.1.1.1 Ground

First, the effectivity of the pigment is dependent on the colour of the ground. Phosphorescent pigment particles are large, which means that you need several layers to optimize their hiding power. It is inevitable that there will be 'dead space' between the pigments, where you can find only pure medium. The energy is distributed most effectively when the ground is white, as it will reflect light back into the paint.[16] When this is the case, the luminescence is so bright that the 'dead space' is difficult to notice with the naked eye. A black or coloured ground will cause the spectrum to be partly or entirely absorbed, decreasing the afterglow considerably.[17] For this research, it was decided to apply the different pigments on a white and a black ground and compare the effects.[18]

2.1.1.2 Filling materials

The standard readymade phosphorescent paint consists of 25% phosphorescent pigment, 55% binder and 20% filling material.[19] The latter is an essential addition, as the phosphorescent pigments are very heavy and without a filling material or thickener the pigment settles in the lower layers of the dispersion. Not all filling materials are suited for this purpose. The most important factor is that

[16] http://glowinc.com/glow-in-the-dark/grainy-issue.aspx (consulted October 2014)
[17] http://www.artemisus.com/content/faq.php (consulted October 2014)
[18] The white ground was the plain pre-grounded canvas board. For the black ground, two layers of black acrylic paint were used.
[19] http://www.artemisus.com/content/faq.php (consulted October 2014)

the material is transparent enough to let light, ultraviolet radiation and the afterglow of the pigments through. When the filling material is too opaque, it will block these kinds of radiation partially or fully, depending on the percentage of added material. According to industry, calcium carbonate (CaCO3) and fumed silica are the two most regularly used materials in the production process of phosphorescent paint. Based on this information, several filling materials with different characteristics have been selected for the tests. All of these materials are part of the inventory of conservation studios. Aluminum hydroxide and calcium carbonate represent the semi-opaque filling material, and Aerosil and glass spheres were added to the test due to their transparency. The opaque titanium dioxide was added for comparison.

2.1.1.3 Daylight colour

The daylight colour of phosphorescent pigments is light yellow, with a trace of the colour of the afterglow. To obtain another daylight colour, the industry does not recommend adding regular pigments or dyes. Due to the tendency of the added pigments and dyes to absorb and reflect parts of the spectrum, less energy will be reaching the phosphorescent pigments. This diminishes the resulting afterglow. Dark and opaque pigments especially, have a negative influence on the phosphorescence.[20] To test this theory the semi-transparent nickel-titanium yellow (Kremer 43200) and an opaque cadmium yellow light (Kremer 21030) were chosen.

2.1.1.4 Pre-treatment

Lastly, the phosphorescent pigments themselves can be treated to manipulate the properties. Two of these tricks have been tested. By grinding the pigment, the particles will become smaller and their phosphorescence will decrease.[21] Another way of manipulating the appearance of the paint is by washing the pigments. When dry phosphorescent pigments are added to a medium (for instance an acrylic dispersion), they will absorb water and ancillary materials. This will result in a dryer and granular paint layer.[22] A day before mixing the paint, you can wash the pigments and make a saturated paste by adding distilled water to the phosphorescent pigments to ensure this does not happen. The paste will also facilitate the dispersion of the pigments in the paint.

2.1.2 Selecting pigments

The majority of the pigments that were selected for the test run, are ZnS based and doped with copper. The choice for these pigments has not been arbitrary. Most of the pigments have a light-yellow colour in daylight and a green-yellow emission spectrum, just like the original artwork. Several pigments from the collection of Riedel-de Haën have been chosen, because research indicated that this supplier may have also made the pigments in Gieses *Wiedolux* paint.[23] To see if it is possible to mix emission spectra, a ZnS pigment with red yellow phosphorescence made by Nemoto & Co., Ltd. has been added. One rare earth metal pigment was manipulated to see how far the long and bright afterglow of the pigment could be weakened with the use of filling materials and/or the pre-treatment of the pigment. For an overview of the selected pigments, see **table 2.**

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[20] *About Photoluminescence. A Brief Technical Introduction*, Baring Technologies P/L, 2011, p.6-8

[21] http://www.artemisus.com/content/faq.php (consulted October 2014)

[22] Keune, P., 'Fosforescerende Verven', *kM* 0, autumn 1991, p.24

[23] The *Wiedolux* paint that Giese used, was made by the firm Hermann Wiederhold KG in Hilden, Germany. At that time, there were very few producers of phosphorescent pigments in the vicinity. The firm Riedel-de Haën was a major manufacturer in Seelze, Germany and therefore it seems very likely that their pigments were used in the *Wiedolux* paint.

Nr.	Kind	Color	Manufacturer	Type
1.	ZnS:Cu	Green	Riedel-de Haën	Lumilux Grün N5 (Effect Green)
2.	ZnS:Cu	Green	Riedel-de Haën	Lumilux Grün N5
3.	ZnS:Cu	Green/yellow	Kremer Pigmente	56500
4.	ZnS:Cu	Green/yellow	Nemoto	GSS
5.	ZnS:Cu	Green/red	Nemoto	GSR
6.	ZnS:Cu	Green/yellow Green/red	Nemoto	GSS/GSR (1:1)
7.	SrAl	Green	Riedel-de Haën	Lumilux SF-N2

Table 2. Overview of the different pigments that were used in the experiment

2.1.3 Selecting a binder

The binding medium has to be as transparent as possible, only then can the radiation reach the pigment and excite the electrons in the pigment in the best way possible. Examples of suitable media for these kind of paints are epoxies, polyesters, nitrocellulose, vinyl, urethane lacquers, oil lacquers and acrylics.[24] Phosphorescent pigments cannot always be added to an arbitrary medium. Some pigments are specifically made for one medium (water based, oil based or solvent based), but others can be added to several binders. The medium that was selected for the tests is the acrylic dispersion Plextol B500, because of the similarities in appearance with the original binder and the availability of the product. Because Plextol B500 is known to be yellow, it would be advisable to use a dispersion that has stable additions for the final retouching medium, to reassure that all the added materials will not negatively influence the longevity of the self-made paint.

2.2 Set up tests

2.2.1 Making swatches

On pre-grounded canvas boards (Talens Amsterdam), swatches of 6 x 5 cm were drawn with a pencil. All the paints were mixed just before application and immediately applied on the corresponding swatch. The percentages of the added materials were equal to those that are usually standard for commercial paints (see paragraph 2.1.1). Since paints that consist solely of phosphorescent pigment and binder are not common in the industry, it was not possible to rely on these percentages. For these paints, a ratio of 1/3 phosphorescent pigment and 2/3 binder was employed. Because the consistency of the different mixtures was variable, not all paints were applied in the same way. A soft brush was used for the mixtures with a low viscosity, working in thin layers until all the paint was applied. For the more viscous paints, a plastic palette knife was deemed more suitable.

2.2.2 Set-up visual test

The swatches were visually evaluated under regular light and UV radiation, and also next to the original artwork for comparison. Aspects that were taken into account were properties such as the colour of the paint in daylight, the colour and intensity of the afterglow, the texture of the paint, the effect of a filling material or regular pigment on the visual properties of the paints etc. The swatches were inspected with the naked eye, a head-lens and a stereomicroscope.

[24] http://www.artemisus.com/content/faq.php (consulted October 2014)

2.2.3 Set-up technical analysis

Even though a lot of information can be acquired by visual analysis of the different phosphorescent paints, it is not possible to make a statement about the quantitative differences in the intensity of the afterglow. This is important complementary information, because it gives an objective insight into the influence of filling materials, pre-treatments etc. on the properties of the self-made paints. To obtain this information, the department of *Optical Sciences* at the University of Twente was contacted. They kindly offered their help which allowed for further tests into the paints to be done.[25]

At the University of Twente, a set-up was made on an optical table on which magnetic bases were stacked so they could hold a swatch and a black passe-partout. The passe-partout was necessary to make sure the sensor would not measure phosphorescence of other swatches. A light source (a KL1500 Schott microscopy lamp) was placed at a distance of 10 cm in front of the swatch. This low-tension halogen lamp (15 volt/150 watt) produces white light with a colour temperature of about 3200 Kelvin. A photodiode (UDT sensors PIN-10D) was placed at 5 cm from the phosphorescent surface. It was placed at an angle of about 45 degrees, so the excitation light would not be blocked. The signal from the photodiode was amplified using a 100MV/A transimpedance amplifier (University of Twente built) and digitized using a National Instruments USB-6212 Data Acquisition card. Each swatch was illuminated for 10 seconds and the decay of the phosphorescence was measured until the signal had dropped below a certain threshold. The optical responses of the various phosphorescent compositions were plotted on a logarithmic scale, in order to show a single exponential decay as a straight line. These curves could eventually be compared to each other, using a curve of the original paint as a reference.

3. Results

3.1 Visual evaluation

The visual characteristics of the different swatches were observed and compared in daylight, in UV light and in the dark. The most notable aspects will be discussed in the following paragraphs.

3.1.1 Ground

The colour of the ground is a decisive factor in the appearance of the paint in daylight. Since the hiding power of the paint is not optimal because of the large pigments, the transparent binder and the translucent pigments, one can see the ground through the paint. When looking at the swatches in the dark, it becomes clear that the colour of the ground is also an important factor in the ultimate intensity of the phosphorescence [Fig.3]. As the theory suggests, a black ground absorbs energy, which results in an afterglow with a diminished intensity and longevity.

[25] My special thanks goes out to Herman Offerhaus, Jeroen Korterik and Dirk Jan Dikken.

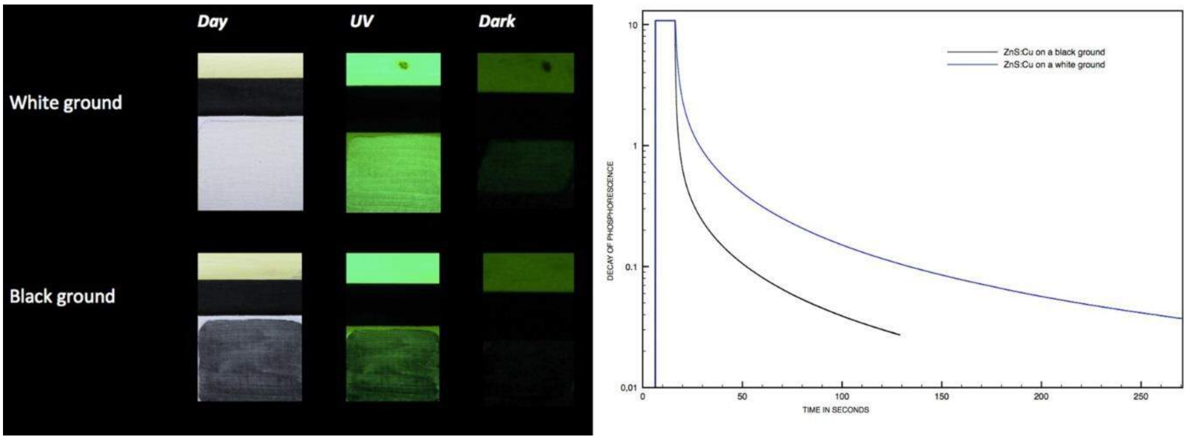

Figure 3. On the left, the visual results of different grounds (experiment 2 and 3, pigment 6). The bar above each swatch is a part of the original artwork, added for reference. On the right, the technical results of different grounds (experiment 2 and 3, pigment 6), plotted against a logarithmic y-axis.

3.1.2 Filling materials

The effect of the filling materials is apparent in daylight and in the dark [Fig. 4]. In daylight, some filling materials influence the colour of the paint. Glass spheres give the paint a greyish shade, and calcium carbonate and titanium dioxide dissolve in the medium and form an opaque beige and white film respectively. The addition of filling materials give the paint a rough and grainy texture that, even when applied in layers, can easily crack or result in air bubbles.

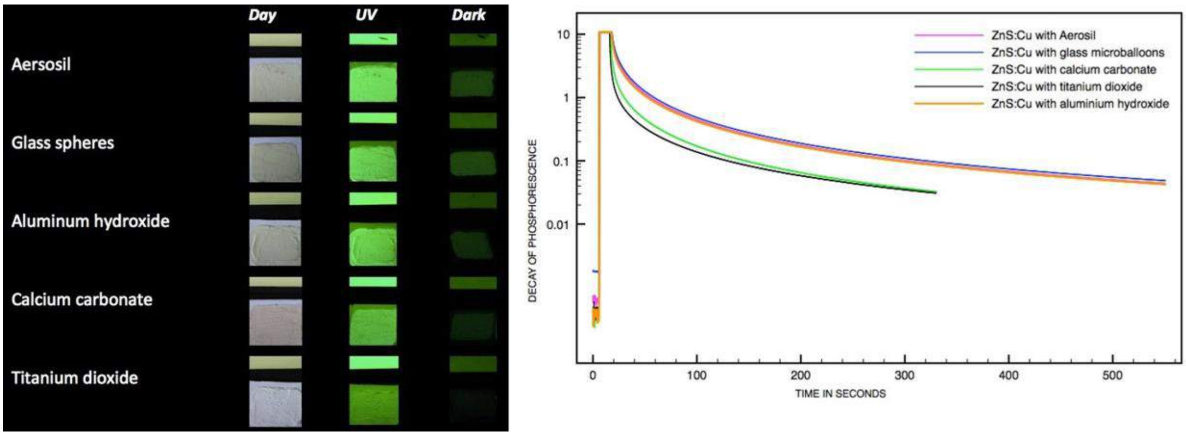

Figure 4. On the left, the visual results of the addition of different filling materials (experiment 4, 5, 6, 10 and 11, pigment 6). The bar above each swatch is a part of the original artwork, added for reference. On the right, the technical results of the addition of different filling materials (experiment 4, 5, 6, 10 and 11, pigment 6), plotted against a logarithmic y-axis.

When you look at the intensity of the afterglow, we can conclude that the semi-transparent aluminium hydroxide has the same translucency for UV radiation as the glass spheres and Aerosil. The often-used semi-transparent calcium carbonate however is just as opaque as titanium dioxide. Both filling materials cause a severely diminished afterglow. The effect of the opaque filling materials seems to be more severe than the effect of having a dark ground.

3.1.3 Daylight colour

Besides the obvious effect of the regular yellow pigments, other effects can also be observed in daylight [Fig. 5]. Just like the filling materials, the addition of regular pigments can give the paint a textured surface. When looking at the effect of the pigments in the dark, there is only a slight difference between the semi-transparent and opaque pigment. Cadmium yellow has the same effect on the phosphorescence as calcium carbonate and titanium dioxide. Nickel-titanium yellow however has semi-transparent properties and therefore has a better emission of electromagnetic radiation. In both cases the phosphorescence is diminished strongly. We can conclude that the right colour of the retouching medium in daylight cannot be attained by using regular pigments, because they will create a ‘veil’ over the phosphorescent pigments. This means that they cannot absorb light very well, which affects the intensity of the afterglow. Only transparent pigments or dyes can be used.

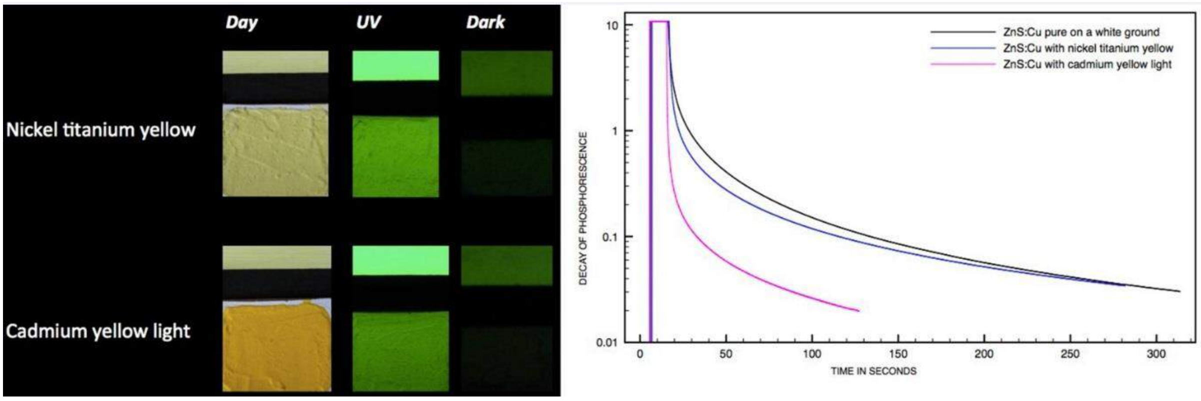

Figure 5. On the left, the visual results of the addition of two regular pigments (experiment 8 and 9, pigment 6). The bar above each swatch is a part of the original artwork, added for reference. On the right, the technical results of the addition of two regular pigments (experiment 8 and 9, pigment 6), plotted against a logarithmic y-axis.

3.1.4 Pre-treatment

The effects of the pre-treatment in daylight, can only be noticed in the swatches with washed pigments. As the theory suggests, the washed sample is more ‘fatty’ and looks like it has more binding medium than one that was not pre-treated. The results do vary per pigment. The pre-treatment mainly influences the properties of the phosphorescence [Fig.6]. The grinding of the pigment does not seem to have any effect on the afterglow. It could be that this is only feasible by using industrial equipment, because the pigments are very hard. The washing however, does affect the phosphorescence. Some pigments have a better afterglow, and all pigments are dispersed better.

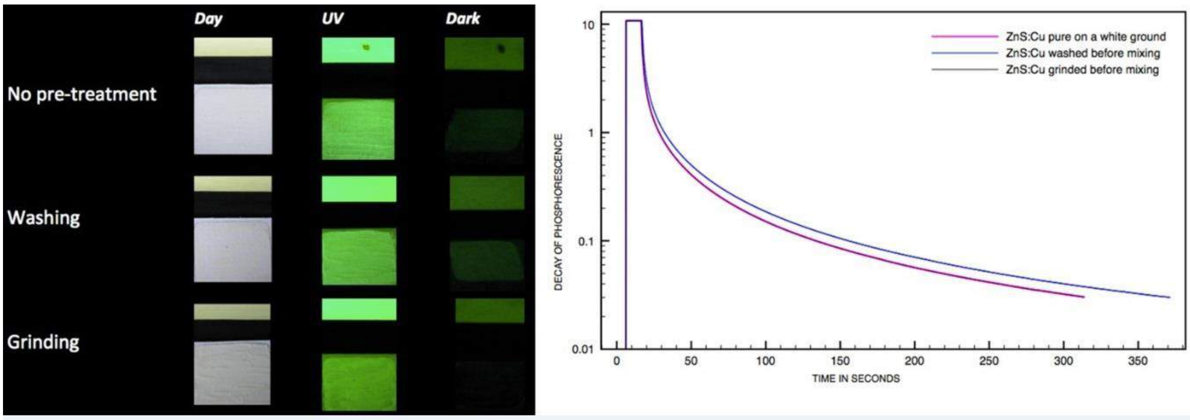

Figure 6. On the left, the visual results of the pre-treatment of the phosphorescent pigment (experiment 1 and 7, pigment 6). The bar above each swatch is a part of the original artwork, added for reference. On the right, the technical results of the pre-treatment of the phosphorescent pigment (experiment 1 and 7, pigment 6), plotted against a logarithmic y-axis.

The reason why the washing intensifies the phosphorescence might have something to do with washing away some (unknown) additions that somehow have a negative influence on the afterglow.[26] To determine what exactly is extracted from the pigments, it is necessary to compare the results of technical analysis on both the unwashed and the washed pigment. Unfortunately, it was not feasible to examine this phenomenon any further within the scope of this research project.

3.1.5 Phosphorescent pigments

As was expected, the properties of zinc sulfide pigments doped with copper came closer to the properties of the original zinc sulfide-based paint than those of the strontium aluminate pigments [Fig. **7**]. None of the tips and tricks of the manufacturers helped to modify the aluminate-based paint in such a way that it resembled the original paint. The maximum duration of the emission of the aluminate is so long and it shines so brightly that it outshines the original paint even in the least favorable situations.

[26] Conversation with Katrien Keune, 19 March 2012

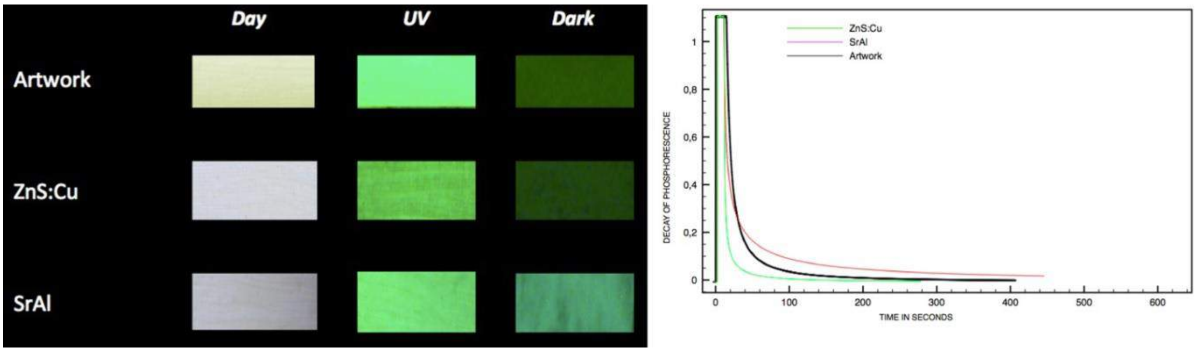

Figure 7. On the left, the visual results of the different types of phosphorescent pigment (artwork vs. experiment 3 with pigment 6 and 7). On the right, the technical results of the different types of phosphorescent pigment (artwork vs. experiment 3 with pigment 6 and 7), plotted against a linear y-axis.

The regular ZnS:Cu pigments have a bright green afterglow, which does not resemble the softer, more reddish afterglow of the artwork. The yellow-red afterglow of the other ZnS pigment however, was too warm in colour and did not match the original paint either. The mix of the ZnS pigments with the green and yellow-red afterglow – both with a light yellow colour in daylight – gave a surprisingly positive result. It is possible to mix phosphorescent pigments with different emission colours and you can play with the percentages of the phosphorescent pigments to determine the final effect. Before the test started, it was assumed that the afterglow would be mixed in a subtractive way, just like light. But it turned out that the optical effect was more comparable with that of mixing colours in an additive way.

3.2 *Technical analysis*

When analysing the emission measurements of the swatches, it became clear that zinc sulphide and rare earth pigments (in this case strontium aluminate) have two half-lives, or periods of time that the phosphorescent paint loses half of its phosphorescence. This phenomenon causes the divide in the curves that are registered with the light sensor. First, the intensity drops in a very short period of time. This usually happens in a virtually straight line on the logarithmic scale. The second part of the graph starts when the first part dropped to almost zero, after which it slowly decreases. In the graph this will be registered as a curve. The sudden drop in intensity and the lingering afterglow can also detected with the naked eye.

The differences between the graphs of the original paint and the self-made paints based on zinc sulphide and strontium aluminate pigments indicate that we are dealing with three very different materials. Of the three paints, ZnS:Cu has the least intense afterglow, followed by ZnS:Ca and strontium aluminate respectively. Even though the graphs of ZnS:Ca and strontium aluminate are comparable, one can technically and visually determine that after an exposure time of more than 10 seconds the strontium aluminate pigments have a much longer and brighter afterglow.

Altogether, most of the results that were obtained with technical analysis of the swatches match the recorded visual characteristics. Through these tests however, the quantitative changes were registered and the subtle changes in the phosphorescence could be perceived very well. The most interesting comparisons between the different graphs, can be found in figures 3 to 7.

4. Conclusion

Because an artwork without title (1968, Rijksmuseum Twenthe, Enschede, Holland) by the German minimalist Rainer 'IMI' Giese needed to be retouched, research was done into phosphorescent pigments and the possibility to compose one's own phosphorescent paint to match the characteristics of the original paint layer. In this case, it became clear that a retouching material needed to be manipulated after technical analysis revealed that the original pigment consisted of ZnS:Ca. These pigments are not on the market anymore because of health and safety regulations.

The search began for a suitable retouching material that has a similar colour as the original in daylight and also has a comparable colour, intensity and duration of the afterglow. Tips and tricks from the paint industry were applied on different swatches and can broadly be divided into the following categories: ground, filling materials, daylight colour, pre-treatment, and different phosphorescent pigments. The results were analysed visually and technically. On the whole the visual evaluations corresponded with the findings in the technical analysis, but in some cases the paints differed less optically than technical analysis indicated.

The ground, filling materials, daylight colour and pre-treatment all have influence on the daylight colour. Since the phosphorescent pigments are translucent and cause 'dead space' because of their size, the colour of the filling material is visible. As expected, adding regular pigments to the paint alters the daylight colour of the phosphorescent paint but some filling materials also change the hue of the paint in daylight. Lastly, and perhaps most surprisingly, washing the phosphorescent pigments before adding them to the binder will make the paint layer look more saturated and glossy.

Filling materials and regular pigments in the self-made paint can result in graininess of the paint layer, when the medium does not wet these materials entirely. Adding a small amount of water to the dry materials to create a smooth paste can prevent this problem. When the paste is added to the other components of the paint, it will result in a better dispersion of the material. The paint must be applied in very thin layers to prevent the occurrence of cracks and air bubbles.

All the categories of manipulation also have an effect of the phosphorescence of the paint. When the ground is black or has a certain colour, the ground will absorb light. Less light is scattered back into the paint layer, which results in a diminished phosphorescence. The semi-transparent and often used calcium carbonate and the tested opaque filling materials have a negative influence on the intensity and duration of the afterglow. The right daylight colour of the retouching medium cannot be attained by using regular pigments, because they will create a 'veil' over the phosphorescent pigments. This means that they cannot absorb light very well, which affects the intensity of the afterglow. Only transparent pigments or dyes can be used. Only the washing of the pigments will increase the intensity of the afterglow of some of the tested materials, most likely due to the removal of an unknown addition that has a negative influence on the phosphorescence. All in all, a black ground and the addition of opaque filling materials seem to have the most severe influence on the properties of the paint.

The phosphorescent pigments that are currently available do not have the same properties as the ZnS:Ca pigments that were found in the original paint layers. The tested zinc sulphide doped with copper has a shorter and less intense afterglow, and also has an emission spectrum that is greener. The strontium aluminate has a much longer and intense afterglow, and also has an afterglow that is too green. The effect of the ZnS:Ca pigments can be imitated by combining ZnS:Cu pigments with a green and a yellow-red afterglow. Further tests indicated that in this case they have to be mixed in a ratio of 1:1, or with slightly more phosphorescent pigment with a yellow red afterglow.

When making a retouching medium for Giese's artwork, all the information gained from these tests will be kept in mind. All the manipulations that will positively influence the phosphorescence will be applied. The mix of glow-in-the-dark pigments with a different colour afterglow shows good results but since these have a pastel colour in daylight, a way of successfully altering the daylight colour had to be found. Because it is not possible to add regular pigments, the industry developed coloured resin micro balloons that would be a good option for this specific case. The colours that are available correspond with the colour of the afterglow, and therefore have a very intense hue. The yellow that is available is not an exact match with the original paint layer, but it does come close. Even though there are complex differences between the material available on the market today and the original paint layer, the tests visually match the artwork enough to be able to restore the geometric unity that Giese had in mind when making this fascinating artwork.

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Links

Artemis US:
http://www.artemisus.com/content/faq.php

Glow Inc:
http://glowinc.com/glow-in-the-dark/glow-in-the-dark-technologies.aspx
http://glowinc.com/glow-in-the-dark/grainy-issue.aspx