USE OF COBALT SICCATIVE IN CONTEMPORARY OIL PAINTING: A STUDY OF ITS BEHAVIOR AFTER ACCELERATED AGEING

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ABSTRACT: *The present paper presents the results obtained after a study of the behavior of oil paint after addition of cobalt siccative in various ratios. This is a procedure particularly used by artists taking part in fast painting competitions, which require fast drying of their work, but also by many artists who shorten drying times of their works by using this substance.*

The study focuses on analysis of color alteration in pictorial layers after being subjected to ageing cycles in a climatic and photo-oxidation chamber. Particular emphasis has been placed on the study of color alteration as it is one of the factors that can affect conceptual aspects of contemporary works. For this reason, a survey was held among many artists, which yielded interesting data on ratios, use, and artistic intentions.

After ageing (exposition to UV radiation for 900 hours and a temperature ranging between 10 and 50º C, with humidity also ranging between 60 and 90% for 500 hours), and having studied behavior through microphotography and colorimetry, it was concluded that UV radiation causes fading in pictorial layers, with most impact on blue tones, and that humidity and temperature ageing slightly darkens colors, placing stress on the priming layer and in tension areas close to the paint.

KEYWORDS: cobalt siccative, oil painting, ageing, contemporary art, artists.

1. INTRODUCTION

Use of cobalt siccative is usual among artists to accelerate the drying process of the works in the case of oil paintings. This paper describes an experimental study meant to analyze the effects, mainly on color, that including these substances can have on pictorial layers, both on the aesthetic and on the conceptual level. For this reason, it has been ascertained through a survey that artists do not usually follow manufacturers' instructions, but rather use too much product, which might increase these effects even more. Thus use of these drying catalyzers might have negative consequences for conservation of these works both on the material and on the semantic level.

Siccatives act as oxygen bearers in the drying process of the oils used in oil painting. They are chemical additives that favor the passage from the liquid phase of paint (necessary for its application) into the solid phase (Gómez, 1998). Siccatives play two roles: they are useful to accelerate the drying of thick pictorial layers, and in the case of oil colors made by artists themselves, they are necessary additives to regulate the drying of their pigments.

The term "siccative" has various meanings, and is used in the literature and by artists themselves with different meanings (Villarquide, 2004). In general, siccatives may be oils that dry by oxidation in the air (historically, oil drying was increased by baking them or by using such pigments as litharge or lead oxide). The term "siccative" can also refer to pigments or metals added to oil to accelerate its drying. In this case, they would catalyze polymerization reactions. There are siccative pigments such as lead, zinc, cobalt, and manganese compounds.
Finally, the term "siccative" can refer to the liquid siccatives added to the pictorial mix or color. These can be diluted in White Spirit® (most frequently), the ratio of solvent being very high and the percentage of metal salts being very low.

Throughout history, the use of other siccatives has been mentioned in various treatises: for example, minium, verdigris, ground glass, pumice, charred bones and zinc sulphate. These substances were added to other pigments with a lower siccative power to accelerate the drying process. Lead-based siccatives were the ones most used until the late 19th century, after which metal combinations were used. In the last third of the 19th century, use of siccative was popularized, and it appeared as a specific product in color merchant catalogues[1]. The most popular product in the late 19th century were the *Siccatif de Courtrai* and the *Siccatif de Harlem*. Harlem and Courtrai siccatives were already mentioned in Robeson's trade documents in 1958, and Harlem siccative is already mentioned in Reeves's catalogue in 1978, and in Windsor & Newton's catalogue in 1883 (Carlayl, 2002).

In analysing the use made by contemporary artists of this kind of means and siccatives, we have found that these two latter product are currently used by a minority only, as it has not been mentioned by the artists who took our survey. And, studying their current composition, we can point out that Courtrai siccative currently contains calcium and zirconium salts, according to the manufacturer *Sennelier*. It can be pointed out that Doerner[3] claims that historically lead-manganese siccative used to be known as Courtrai siccative.

By contrast, the siccative medium Harlem Duroziez contains formo-fenolic resine, linseed oil and petroleum essence according to the manufacturer *Lefranc-bourgeois*. Its composition does not include cobalt. Doemer (2005) claims that it was not really a siccative but rather an oil-resin compound. Church (1915) also mentions that the composition of Harlem siccative also included resin.

Furthermore Villarquide (2004) locates the first use of cobalt siccative in France in 1852. Mayer (1988) locates it in Belgium in the same year. As for its composition, this siccative displays an approximate metal content of 6%, constituting cobalt naphtenate.

Cobalt siccative is mainly composed of benzene derivatives, metal salts (cobalt, zinc, and calcium salts) and White Spirit® as the main solvent. It is a blue-violet liquid substance, with a characteristic petroleum-like smell due to its high solvent content. The metal salts in its composition are metal ions (cobalt, zirconium, zinc, and calcium), which react with oxygen. Both cobalt siccative and the Harlem siccative medium dry on the surface and can be used in glazes, whereas Courtrai siccative dries in depth and has the drawback that it provides color to the surface.

Liquin®, a liquid alkyd medium, not very glossy, which increases the fluidity and transparency of oil paint and is manufactured by *Windsor & Newton* is also commonly used as additivie of oil painting.

Our paper focuses on the study of the behavior of the cobalt siccative made by the manufacturer *Titan*®, as it is very frequently used, according to artists themselves. We will leave the study of the behavior of the Harlem Duroziez siccative medium, Courtrai siccative, and Liquin® medium for future papers.

Having performed a survey among fifty artists taking part in fast painting competitions, we obtained a reference for the additives most frequently used currently. Cobalt siccatives top the list, followed by Liquin® medium and the medium manufactured by *Talens*®.

As regards the transformation of work finishes, and given that their final aspect has great importance for artists, and given that use of cobalt siccatives may have an impact on final appearance, we believe that it is important to study possible modifications in the appearance of paintings resulting from use of this siccative. Artists should be informed in order to make decisions on their use.

As for the oil drying process and oil interaction with siccatives, the latter act as oxygen bearers, accelerating oxidation of the reactive double bonds in the linoxyn film that characterizes oil painting (Gomez, 1998). As regards the yellowing of oil-based paintings, Mallégol[9] states that "the level of yellowing is linked to the drying and seems to be affected by temperature rises and the addition of siccatives or linoleates". After reviewing the bibliography on the topic, we found some papers on oil layer ageing, the most outstanding ones being (Erhardt et al, 2005: Robinet and Corbeil, 2003: Keune, 2005: Wexler, 1964).

Concerning cobalt siccative use concentration, and analysing the technical sheet provided, it can be seen that the concentrations recommended by the manufacturer *Titán*® range between 0.5% and 5%. The manufacturer specifies that use above 5% of cobalt siccative can lead to cracks and darkening of the paint. However, there are discrepancies, as the artists interviewed claim to use it in a 10% ratio, thus considerably increasing the recommended siccative ratio. For this reason, our study has also analyzed the behavior of cobalt siccative when applied at a high concentration (10%), as well as its application as varnish, as this mode of use has also been mentioned by artists.

Other sources recommend adequate concentrations. Thus, Mayer (1998) recommends adding the least possible amount of cobalt siccative and specifies that commercial liquid siccatives include a very small amount of metal active ingredients. Erhardt, Tumosa and Mecklenburg (Erhardt, Tumosa, y Mecklenburg, 2000) recommend adding 0.3% to the oil as an effective ratio, accepting its use up to 1%. Rutherford [13] recommends in his patent use between 0.05% and 2% by weight.

One of the first studies on this topic appears in Rutherford (1944), due to the cobalt siccative patent published, which specified that the most damaging component in the siccative is metal salt, that is to say, the active component in the product, which caused a change in color in contact with the air (patent number: 2360283, presentation date: 27th August 1938, issue date: 10th October 1944).

2. AIMS OF THE PAPER

A key aim of the paper was to study and determine the effect of siccative in oil painting, both in the ratios recommended by manufacturers and in higher percentages.

The aims of this research mainly concern quantification of use of siccatives in current oil painting, analyzing the extent to which its inclusion in pictorial layers has become generalized, and studying the application method used by artists. In our case, we believed it was important to perform the study after interviewing a high number of artists, in such a way that we could approach the reality of painting, obtaining data on siccative use, its aesthetic properties, and possible degradation effects. Another aim of our research has also been to bring the world of conservation to that of creation.

Yet another aim of this paper is for the information obtained to reach artists through as many channels as possible, so that they can make relevant decisions on siccative use.

The study started with the design of a survey aimed at artists, which included specific questions on use of drying accelerators. Fifty artists in the current Spanish art world were interviewed. The main criterion to select the population sample was that the artists being interviewed would have taken part in fast painting competitions, as these artists regularly use cobalt siccatives to accelerate paint drying, and thus were are useful source of information. The survey was conducted via Internet as well as in person.

On the basis of the answers given, frequent commercial makes were specified, both for oils and for siccatives, their application method, ratios used, effectiveness… All this information was applied to design the experimental models.

Finally, all the information generated was included in a database to make searches easier.On the basis of this information various experimental models or test tubes were created, which were subjected to several accelerated ageing cycles in order to study the later effect of deterioration agents on pictorial layers. This study was carried out using a spectrophotometer, macro and microphotography, as well as comparison between the stages before and after artificial ageing.

3. SURVEY: POLLS AND INTERVIEWS WITH FIFTY CONTEMPORARY ARTISTS.

The design of the interview that was completed by the artists included such aspects as the artist's education, whether the artist is self-taught or has a formal education, the artist's age, the oil paint brand used, whether siccatives are used or not in the artist's works, and if so, what type of siccative and in what ratio, whether changes are observed in the works as a result of siccative use, whether siccative is used as varnish, whether the artist regards its use as effective, and finally, whether the artists has found cracks, yellowing or darkening in the pictorial layers as a result of siccative use.

Most of the artists interviewed (82%) had had formal education. The age range is wide, as artists still in training have been included in addition to more widely experienced artists. 58% of those interviewed are men, and 42% women. The population is constituted of Spanish artists all over Spain.

As regards the oil paint brands used, most of the artists mentioned *Titán* as the top brand, at 40%. 26% use *Titán* as well as more affordable second brands such as *Rembrandt, Van Gogh,* and *Talens*. The remaining 34 % of artists only use cheaper brands (*Garvi, Pizarro, Amsterdam*).

Of the 50 artists interviewed, 21 use a siccative, and the rest do not.

For the most part, use of siccatives is not widely spread among Fine Arts students. Fine Arts students are those taking a B.A. university degree, that is to say, students with the highest level of training in the creative domain.

Artists who use siccative are not restricted to cobalt siccative. Thus, according to the survey, its use can be quantified: 43% of the artists interviewed use Liquin®, 47 % use *Titán* brand cobalt siccative, and the remaining 10% use *Talens* medium.

Use of siccative is intended to accelerate drying in specific impastos, or to make oil paint more fluid.

As regards the method of application of any of the previously mentioned siccatives, 81% of the interviewed artists mix it with the oil paint in the palette, almost always using a variable ratio. The remaining 19% use it as varnish.

As for the degree of artists' satisfaction with use of siccative, for 47.6%, almost half the artists, it provides a good result. For 19%, it provides an acceptable degree of satisfaction, and the remaining 33% have not considered the issue.

As regards siccative alteration, 14.3% answered that cracks appear, 19% that yellowing takes place, 57.14% that they did not know what effect it might have, 4.7% that it has faded with time, and the remaining 4.7% that it makes the canvas matte after drying.

There are all highly significance issues, as they affect work finishes, and thus sometimes the artist's intentions. Transformation of pictorial surfaces is usually a negative aspect of use of these products, as they depart from the artist's initial intentions.

4. EXPERIMENTAL

As regards the set of instruments used in the experiment, an artificial ageing chamber accelerated by radiation UV was used, whose dimensions are: 30 cm. X 40 cm x 70 cm and which has Philips special Hg. ALTINIC BL TL 20W light tubes inside, with no special filters.
As for the accelerated chamber for ageing by humidity and temperature, it is the DYCOMETAL Dl-100 model.

Possible color changes in different experimental models were measured with a Minolta CM-2600D spectrometer, using CIE D56 illumination conditions (daylight, color temperature 6500° K) and the 10º standard observer. Data were taken using a specular component included (SCI) which minimizes the influence of measurement surface conditions and specular component excluded (SCE), which corresponds more closely to professional visual evaluation.

The various micrographs were taken using a Leica Binocular magnifier S8APO.

We also used a digital camera Nikon D-40 for macro photos, and 52-m 1, 2, 3 Kenko close-up lenses.

The study was designed to examine the influence of various cobalt siccative ratios mixed in the same amount of oil in the different colors. The cobalt siccative used was chosen due to the result of the survey conducted prior to artists. The cobalt siccative used was that marketed by the manufacturer *Titán®*

We chose a 100% cotton, commercially primed *Taker* canvas, as well as *Titán®* oil paint as the materials to simulate a real painting. Again, this choice was motivated by the results of the survey among artists, which indicated that these materials were the most commonly used ones.

We chose a color range corresponding to the basic painter's palette (titanium white, ivory black, natural sienna, cobalt blue, medium cadmium yellow, and scarlet red).

The canvases which would serve as the experimental model were primed, designing some frames over the priming in which different oil colors were applied. To these colors a greater amount of cobalt siccative was gradually applied, exceeding in one of the frames the amount specified by manuals and manufacturers. This was done to test the effect of random excessi amounts which artists might use.

Test tube preparation process: a first oil layer was applied to prime the surface, and then the brush was loaded with paint, which was spread up to the band which served as a divider to obtain a flat surface which would make it possible to measure color. Oil paint was directly taken from the tube, and insistently mixed with the siccative. Siccative ratios in each frame were determined by the percentage range recommended by the manufacturer Titán – between 0.5% and 5% – applying a 10% ratio to one frame in order to study what might happen in case of excess application, and applying siccative as varnish in another frame.

Six frames were made for every color: the first one for oil paint with no siccative, the second for a mix of 10 ml. oil paint plus 0.25% cobalt siccative. In the third frame, 10 ml oil paint was mixed with 0.5% cobalt siccative. In the fourth frame, 10 ml oil paint was mixed with 5% cobalt siccative. In the fifth frame 10 ml oil paint was mixed with 10% cobalt siccative. Finally, in the sixth frame the siccative was superficially applied as varnish, with no control of its ratio, as some artists had claimed to do. Both the oil paint and the siccative were measured in ml, using a graduated test tube.

As regards sample drying times, the influence of cobalt blue pigments on the drying speed of oil films has been compared to that of cobalt octanoate, increasing drying speed together with product concentration. Thus, the drying of cobalt octoanate might be analogous to that resulting from cobalt blue pigment.

Drying times for each frame in our experimental models are described in the following table:

Tabla 1. Table summarizing drying times for color layers depending on their respective siccative ratios

	SAMPLE COMPOUND	DRYING TIME
1	Titanium white layer, 10 ml white oil paint with no additives.	Sticky 2 days after application. Dry to the touch after 5 days.
2	Titanium white layer (10 ml), plus 0.5% siccative (3 drops).	Dry to the touch, no staining, after 24 hours. Dry with no staining after 48 hours.
3	Titanium white layer (10 ml) plus 2.5% cobalt siccative (6-7 drops).	Completely dry in 24 hours.
4.	Titanium white layer (10 ml) plus 5% cobalt siccative (20 drops).	Completely dry in 24 hours.
1.	Titanium white layer (10 ml) plus 10% cobalt siccative (40 drops).	Completely dry in 24 hours.
2.	Titanium white layer with cobalt siccative as varnish.	Completely dry in 5-6 hours.
3.	Ivory black layer, 10 ml ivory black oil paint with no additives.	Sticky after 24 hours. Stains, but almost dry after 46 hours.
4.	Ivory black layer (10 ml) plus 0.5% cobalt siccative	Sticky after 24 hours. Stains, but almost dry after 46 hours.

	(3 drops).	
5.	Ivory black layer (10 ml), plus 2.5% siccative (6 drops).	Sticky after 24 hours. Slightly stains, but almost completely dry after 46 hours.
6.	Ivory black layer (10ml) plus 5% siccative (20 drops).	Sticky after 24 hours. Dry to the touch after 46 hours. .
7.	Ivory black layer (10ml) plus 10% siccative (40 drops).	Almost dry 24 hours after application, but still stains. Completely dry after 46 hours.
8.	Black with superficial cobalt siccative as varnish	Completely dry in 6-7 hours.
9.	Natural sienna layer (10ml) oil paint with no additives.	Dry to the touch in 48 hours.
10.	Sienna layer (10 ml) plus 0.5% cobalt siccative (3 drops).	Dry to the touch in 48 hours.
11.	Sienna layer (10 ml) plus 2.5% siccative (6-7 drops).	Dry to the touch in 48 hours.
12.	Sienna layer (10 ml) plus 5% siccative (20 drops).	Dry to the touch in 48 hours.
13.	Sienna layer (10 ml) plus 10% siccative (40 drops).	Dry to the touch in 48 hours.
14.	Sienna layer with superficial cobalt siccative as varnish.	Completely dry in a few hours (approx. 5 hours)
15.	Cobalt blue layer (10 ml) oil paint with no additives.	24 hours after application, cobalt blue is wet, but completely dry after 72 hours.
16.	Cobalt blue layer (10 ml) plus 0.5% siccative (3 drops).	24 hours after application, sticky but almost dry. After 72 hours, completely dry
17.	Cobalt blue layer (10 ml) plus 2.5% siccative (6-7 drops).	24 hours after application, remains sticky. After 72 hours, completely dry to the touch.
18.	Cobalt blue layer (10 ml) plus 5% siccative (20 drops).	24 hours after application, completely dry
19.	Cobalt blue layer (10 ml) plus 10% siccative (40 drops).	24 hours after application, completely dry
20.	Cobalt blue layer with superficial cobalt siccative as varnish.	Completely dry in 6-7 hours.
21.	Cadmium yellow layer (10ml) oil paint with no additives.	24 hours after application, the layer remains wet. After 72 hours, the layer is completely dry.
22.	Cadmium yellow layer (10ml) plus 0.5% de siccative (3 drops).	24 hours after application, the layer remains wet. After 72 hours, the layer is completely dry.
23.	Cadmium yellow layer (10 ml) plus 2.5% siccative, (6 -7 drops).	After 24 hours, the layer is dry to the touch.
24.	Cadmium yellow layer (10 ml) plus 5% siccative (20 drops).	After 24 hours, the layer is dry to the touch.
25.	Cadmium yellow layer (10ml) plus 10% siccative (40 drops).	After 24 hours, the layer is dry to the touch.
26.	Cadmium yellow layer with superficial cobalt siccative as varnish.	Completely dry in a few hours (approx. 5 hours).
27.	Titan scarlet red layer (10 ml) oil paint with no additives.	48 hours after application, the layer remains sticky.
28.	Titan scarlet red layer (10 ml) plus 0.5% siccative, (3 drops).	48 hours after application, the layer is completely dry.
29.	Titan scarlet red layer (10 ml) plus 2.5% siccative (6-7 drops).	48 hours after application, the layer is completely dry.
30.	Titan scarlet red layer (10 ml) plus 5% siccative (20 drops).	48 hours after application, the layer is completely dry.
35.	Titan scarlet red layer (10 ml) plus 10% siccative (40 drops).	48 hours after application, the layer is completely dry.
36	Titan scarlet red layer with superficial cobalt siccative as varnish.	48 hours after application, the layer is completely dry.

Once the samples were completely dried, they were subjected to ageing cycles. The programmed cycle in the accelerated ageing chamber subjected samples to certain humidity and temperature conditions and was repeated every twenty-four hours. The cycle chosen for accelerated ageing by temperature ranged during that time between 10º C and 50º C. These extreme oscillation conditions were established in order to generate appreciable variations in the samples. Humidity also ranged, over the 24 hours, between 60% RH and 90% HR. Finally, samples were subjected to these conditions for 500 hours.

Furthermore, the ageing established for UV radiation consisted in subjecting the samples to a total of 900 hours' exposure to light at ambient temperature. Samples were placed inside the chamber at a distance of 26 cm with respect to the UV tubes, and received 2150 mW/cm^2.

The macroscopic study consisted in the photographing, using a digital camera, close-up lenses and visible light, of each of the frames or tests, before and after ageing, in order to compare the different results.

The macroscopic study also consisted in the systematic taking of photographs of the various frames observed through the binocular magnifying glass, before and after accelerated ageing, in order to appreciate any possible changes or pathologies which might have appeared. Disassembling the frames was not necessary, as they were relatively small and could be adapted to the magnifying glass base. In this way, no added tension was added after extraction from the chamber.

A comparative colorimetry study was performed on each of the frames before and after ageing. To this end, measurements were taken using the Minolta CM-2600d spectrophotometer on each of the colors and siccative ratios, three times each and on the same point, thanks to a perforated acetate sheet, in order to remove any possible measurement error. The average and standard deviation were calculated on a spreadsheet, to make operation calculation on the basis of the values obtained with the spectrophotometer easier.

5. RESULTS AND DISCUSSION

5.1. Study of the mechanical behavior of the pictorial layers depending on the increase in the siccative ratio.

In trials under UV exposure, it was observed under a stereomicroscope that in some areas light and heat had caused stress in the canvas, resulting in the appearance of small cracks in the priming layer. These cracks did not reach the paint layers. Generally, in all siccative ratios and in all colors after UV ageing, the initial smooth appearance remained the same in the pictorial layers, and no cracks were found on the painted surface.

It should be noted that in experimental tests under T and RH, cracks in the canvas appeared in both directions, invading both the priming and the pictorial layers. In this type of ageing, not only did cracks appear in the priming, as happened in the experimental tests by UV exposure, but these cracks were also more significant, as there were more of them and they reached all pictorial layers.

As regards the addition of cobalt siccative, it was observed that the appearance of cracks in the paint layer was not related to its presence or absence, as no deep cracks appeared in frames which had no siccative. These cracks cannot be attributed to the presence of siccative in the mixture, but rather to the stress experienced by the pictorial layers as a result of changes in humidity and temperature. Furthermore, cracks affected at all concentrations and all colors in a general manner, so that their appearance could be attributed to the dimensional changes in the canvas, rather than to the siccative action [FOT 1 y 2].

Figura.1 White. Frame no cobalt siccative after ageing for HR and T. A large crack in the paint layer can be observed.

Figura.2 White with 10% siccative. Cracks appear in the paint layer after ageing by HR and T.

5.2 Study of the colorimetric tendency of oil layers depending on the increase in the siccative ratio.

Macroscopic study after ageing. In UV ageing it was observed, by comparison to non-aged samples, that cobalt blue frames were noticeably discolored. In addition, they had lost all their gloss, so they looked completely matte. As for titanium white frames, they were discolored and yellows had shifted to a more orange color.

In ageing by moisture and temperature, it was observed, by comparison to non-aged test tubes, that oil grooves had appeared around the frames. The oil had also stained the back of the canvases [FOT 3, 4 y 5].

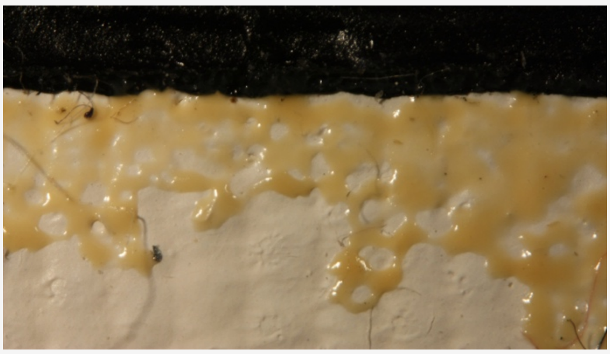

Figura 3. Appearance of oil grooves in the perimeter of the color frames after ageing by HR and T.

Figura 4. Appearance of oil grooves in the perimeter of the color frames after ageing by HR and T.

Figura 5. Appearance of oil grooves in the perimeter of the color frames after ageing by HR and T.

As for the frames to which 10% of cobalt siccative had been added and in which the siccative was superficially applied, the surface had become matte. The colors had turned a more orange and matter in some areas of the surface, and the blues had grown lighter. Finally, the original purple warmth became bluer.

Colorimetry study. Comparison between colors.

The following is a selection of the most relevant and significant data obtained from the samples subjected to ageing by UV exposure.

The greater increase in lightness (ΔL*) or, equally, the greater variation in brightness, was found to a considerable extent in blue, with an average of ΔL*35, as opposed to ΔL*0.1 in yellow or ΔL*2 in white which remain practically the same.

By contrast, in the case of increase in chroma (ΔC*), the greatest difference in chroma was displayed by red and yellow, with a value around ΔC*33. The least difference corresponds to black ΔC* 8 and white ΔC*1.24.

Finally, the increase in hue (Δh*) is more pronounced in black, with a rather high value Δh*22.1, as opposed to Δh* 2 in yellow.

Having observed the increase in total color in each of the colors tested with different siccative ratios, the case of titanium white should be pointed out, where a siccative ratio higher than specified by the manufacturer caused color changes.

In brown, color was altered due to the siccative, but there are no remarkable changed between the various siccative ratios. In cobalt blue, the increase in ratio and application as varnish leads to greater alteration in color, in this case, to its fading. In yellow, the frame without siccative was the one which was best preserved. In scarlet red, the frame without siccative was the one which was best preserved.

The following is a selection of the most relevant and significant data obtained from the samples subjected to ageing by HR and T.

The greatest increase in lightness or ΔL* was found in yellow and blue, the colours which darkened most, at around ΔL*2.4. The colours which darkened least were black and sienna, at around ΔL*0.4.
The greatest difference in chroma was found in blue, with a loss of ΔC*11.8. Red and white are in another group at ΔC* 4.5. Finally, black and brown varied least as regarded their chroma at ΔC* 1.4.
Finally, the increase in hue (Δh*) is again most remarkable in black, Δh*24.7 as opposed to Δh*0.75 in red and Δh* 0.8 in yellow.

In humidity and temperature ageing, and observing the increase in total color for each of the tested color and the various siccative ratios it is remarkable that in the case of titanium white, siccative did not excessively alter color. In the case of black ivory, values are close to 0, that is, there were practically no changes. In cobalt blue, siccative protects, given that the frame displaying the greatest difference has no siccative at all. In yellow, siccative acts as a protector, the sample with no siccative is that one that has changed most. Finally, in red, siccative acts as a protector, as there is a relationship between the increase in siccative ratio and the decrease in color alteration.

Study of the effect of increasing the concentration of siccative in different colors.

We will now examine the total increase in color (Δ E) for each of the colors tested by exposure to UV ageing. This study was conducted on the basis of the increase in siccative concentration.

Titanium white showed an increasing trend in total color deviation as siccative concentration increased. In the case of application as a varnish, discoloration is high, although slightly inferior to that produced by 10% concentration. In the case of black ivory, in ultraviolet UV ageing, there was no alteration as a result of different amounts of siccative: the alteration was quite sharp, but the graph is not linear.

In the case of sienna, natural ageing was slightly accelerated by increasing the concentration of siccative. The graph is linear and upwards, as in the case of titanium white.

In the case of cobalt blue, increasing the concentration of siccative increased the total color deviation. However, the greatest change took place when there was no siccative and the lowest when the siccative was applied as a varnish.

Yellow underwent a higher deflection as the concentration of siccative increased. The largest increase took place when the siccative was applied as a varnish. Note that with a 5% siccative concentration, the opposite trend appears, which is repeated in the case of the aged samples by exposure to HR and T. This suggests that perhaps this specific deviation is due to a problem of in sample execution. In the case of scarlet, behavior is very similar in all siccative concentrations, although total color deviation is slightly lower the more concentrated the siccative, breaking the trend for this color.

Then the total increase in color (Δ E) was studied for each of the colors tested for ageing by exposure to RH and T. Again, the study was conducted on the basis of the increase in siccative concentration.

In the case of titanium white, a greater deviation took place when siccative concentration increased, the highest total deviation corresponding to application of a siccative coating as varnish. Ivory black practically did not change, although the highest degree of deviation was observed when the siccative was applied as varnish. As for sienna, it did not display a behavior that was linked to siccative concentration, and the graph is not linear. In the case of cobalt blue, total color deviation is much higher where there is no cobalt siccative. As concentration increases, siccative total color deviation is lower. This trend is the same in the case of yellow.

Finally, in the case of scarlet red, the process described above was repeated: increasing siccative concentration was associated with a lower degree of color deviation.

Analysis of loss of brightness as a function of the increase in siccative concentration in different colors.

When using the SCI mode (specular component included) for with spectrophotometer measurement, the specular reflectance and diffuse reflectance are included in the measurement process. This type of color evaluation measures the overall appearance, independently of surface conditions. With the SCE (specular component excluded) mode the specular reflectance of the color measurement of samples is excluded. Only scattered light (reflected light in all directions) is measured, which results in an evaluation of color as the observer would see the surface.

Our study was performed on both color measurement systems, and slight color differences were detected between different colors depending on whether the SCI or SCE system was applied.

We wanted to take the final appearance of the surface into account, as well as its relation to the aesthetic values of the work. For this reason, we decided to analyze the total color difference in SCE mode for each type of ageing. The result was that samples which became most matte were those with a higher concentration of siccative (10%) and those in which the siccative was applied as a varnish.

6. CONCLUSIONS

Cobalt siccative is currently the siccative most frequently used to accelerate drying in oil paintings, ahead of Talens® medium and Liquin® alkyd medium.

Cobalt siccative is mostly composed of a solvent such as White Spirit® and cobalt metal ions dissolved in it, which cause a catalyzing reaction in the oil fatty acids, making it possible for oxygen to enter the paint, which thus dries sooner.

As regards cobalt siccative use, nowadays it is generally better known and more used by experienced artists than by Fine Arts B.A. and M.A. students. Almost half of the artists interviewed knows or has used cobalt siccative, which in the Spanish market is marketed by the manufacturer Titán®. Furthermore, most of the artists interviewed use the siccative mixed with oil paint in the palette.

Following the macroscopic study of UV radiation aged models, all cobalt blue, sienna and scarlet red frames display loss of gloss. This behavior, resulting from UV radiation ageing, is also referenced for various colors in Marengo. On the other hand, blues become considerably lighter.

After humidity and temperature ageing, there was a loss of gloss in the frames in which 10% siccative had been added and in which it had been applied as varnish.
In the microphotography analysis, cracks are not related to the increased siccative ratio or to the texture. They are related to ageing-derived tensions (in humidity and temperature samples cracks appear in priming and pictorial layers).

In UV radiation aged samples smaller and more isolated cracks can be observed. The colorimetry study focused on models subjected to UV radiation ageing shows that siccative does not excessively alter white or sienna, and acts as a protector for cobalt blue.

Following humidity and temperature ageing, siccative does not excessively alter titanium white, ivory black, or yellow. Finally, it should be pointed out that on a mechanical level there has been no increase in cracks corresponding to an increase in siccative.

As regards drying times for color layers, it should be pointed out that low concentrations have achieved the same effect as high concentrations, and so excessive use of the product would be unnecessary and damaging for oil paint layers. A 2.5% concentration seems to have the same effect as higher concentrations in most colors. Artists should know this fact, in order to avoid adding more of siccative.

In considering the total deviation of the various colors, it is generally observed that the total deviation is greater by UV ageing for HR and T, and in the case of UV ageing is directly related, in most cases, with the increasing the concentration of siccative. In the case of ageing HR and T, the behavior is uneven colors, although some decrease siccative increased total color deviation.

One of the most interesting aspects of the study is the transformation of oil layer surface finishes. Selection of these finishes is usually a process deliberately performed by the artist, not a random one, and which usually has implicit semantic messages pertaining to the work's message and plastic vocabulary. One of the most significant conclusions, which generally affects all the tested colors, concerns use of siccative in high proportions. This excessive use can make colors matte, affecting their gloss and thus the final appearance of the work. This transformation can take place with no previous knowledge on the artist's part, and thus the condition of the work and its meaning might contradict each other in the future[8]. Artists usually select the finish for the surface or their works by choosing between matte, glossy, or satin, and sometimes even determine a priori the kind of finish for different areas in the same work. However, they use siccative in high proportions or as varnish, methods of use which effect changes in the pictorial layers. This element of plastic vocabulary is a significant part of the artist's intention, and so its alteration may affect the work's message.

It has been established that excessive use of siccative may alter the surface of the picture and thus have an impact on substantial values of the work. As regards conceptual aspects, those concerning their aesthetic and semantic values, it can be said that fading of oil paint is irreversible, undesired by artists, and cannot be corrected by means of later varnishing. For this reason, ageing of paint and its behavior due to the addition of cobalt siccative might in the future lead to discrepancies between the condition of the painting and its meaning. Thus, gradual distancing from the pristine appearance established by the artist may in the future oppose the condition of the painting and its meaning, generating conceptual discrepancies which might force restorers to act.

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