THE TOUCH OF MODERN MATERIALS' ARTISTIC TECHNIQUES

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INTRODUCTION

Artists' desire to experiment with new materials made them introduce in their work nitrocellulose-based colours, alkyd resins, polyvinyl acetate resins, acrylic resins which appeared throughout the 20th century. The acrylics were used both as medium and binders, colours and varnishes. Some artists remained faithful to the oil-based colours that offered the possibility to reapply paint layers, but most turned to acrylic for the short drying time and flexibility.

Plastic, and then celluloid entered the world of visual arts as modern materials which started to be used widely as a substitute for expensive natural materials or difficult to procure (ivory, antler, turtle shell, amber). Celluloid, the commercial name for nitrocellulose, was obtained by mixing cellulose nitrate with an alcoholic solution of camphor. Celluloid was the first transparent and flexible synthetic material that could be used as photographic film and as tape for film rolls. Another product, successor of the celluloid, was the cellulose acetate known as Secoid. This appeared at the beginning of the 20th century and based on its endurance and increased transparency was used to obtain consumables. Phenolic resin Bakelite was introduced in the 20s and used to obtain small-sized objects. In the 20th century [1], starting with the 1935, new plastic materials were introduced such as Styrofoam, PVC (polyvinyl chloride), acrylic, polyurethane, epoxy, cellophane, nylon, synthetic gums.

The synthetic materials were used by artists either as support for a work of art or as a substitute for traditional natural materials. These synthetic materials have begun being manipulated chemically in order to obtain paints and varnishes. The first synthetic paints were obtained from nitrocellulose or by adding alkyds in the traditional oil paints and have become known as polishes or enamels. These dry faster than traditional oil colours and can be used mixed with oil, fact that determined that period's artists to include them on the palette of their innovations. The acrylic colours produced first time by Bocour Colors in the late 40s and the beginning of the 50s represented one of the main innovations in the field of materials for artists. These first colours were in fact acrylic resins, commercially known as Magna. They were obtained by dispersing the pigments in n-butyl methacrylate and diluted in turpentine, alcohol, xylene and toluene. The colours dry fast and form a resistant film that does not turn yellow. In 1950, small quantities of wax were added to their composition.

Towards the half of the 50s the acrylic emulsions developed and were taken as painting materials by numerous artists as Andy Warhol and Helen Frankenthaler. Known as acrylics, these emulsions are very versatile as far as texture, gloss and thickness. They can be diluted in water instead of turpentine or alcohol, dry fast and unlike the acrylic resins they do not solubilize when adding a new paint layer. This allows the artist to paint layer over layer without ruining the previously applied colour. The acrylics do not modify paper or textiles chemically, offering the possibility to use various painting supports. Besides the large variety of colours, the acrylic emulsions could be used as transparent mediums, gels, pastes and varnishes and also as a material for the preparation layers such as ground coat (gesso). Anselm Kiefer developed further the application of acrylics using them to obtain a synthetic gesso resulting in a high mountain top placed in the center of his work Wild Emperor (1975). The transparent varnishes could be mixed with pigments or used as such as final protection, being available both glossy and mat. Even though in time numerous colours based on different synthetic resins have appeared, their commercialization was not successful and they rapidly disappeared from the market. The only product that lasted and has PVA (polyvinyl acetate) in its composition is known as Flashe and it is commercialized by Lefranc & Bourgeois and the only alkyd colours on the market appeared in 1970 under the label of Winsor & Newton and the commercial name of Griffin [2]. The optical, physical and chemical properties that made the acrylic adequate in their use as mediums and coatings were studied by Schupp in 1993 and among them there are: transparency, flexibility, glossiness, good adherence to non-oily surfaces, fast drying, increased endurance and stability under thermic exposure, light and UV radiation over 300 nm.

The direct comparison between oil and acrylic paints created many disagreements, starting from the idea that the acrylics represent a substitute of the oil paints. Each offers both advantages and disadvantages that serve the artist's needs and his technique. It's more equitable to refer to the two materials as two different classes of materials, each having its own medium and specific way of application.

In order to understand the way the synthetic colours suffer degradations in time it's necessary to know their chemical composition and the classes to which they belong. The synthetic mediums used as modern materials include acrylic, polyvinyl (PVA) and alkyd colours. Besides the current use of these new painting materials, the artists continued to use oil and more rarely the synthetic resins, nitrocellulose, polyurethane, epoxy resins and silicone.

ACRYLIC RESINS

All the acrylic products used in the artistic field are acrylate polymers and methacrylate monomers, though sometimes, small quantities of acrylic monomers are added to increase the adherence to the surface [2]. The thermoplastic acrylics used in colours and varnishes are available in two forms: acrylic solutions and acrylic emulsions. The solutions contain an acrylic polymer solubilized in an organic solvent which for the commercial products resumes to white spirit. On the other hand, the acrylic emulsions represent a two-phased system in which the indissoluble acrylic polymer is dispersed in a hydrous solution and stabilized with a surfactant. These are molecules with one hydrophobe part that is chemically connected to a hydrophile part and thus being capable to interact physically with both phases, acrylic and hydrous. The utility of a certain acrylic polymer as a medium or varnish is determined mostly by the physical properties, particularly by those that influence its flexibility and rigidity. These factors are influenced by the polymer's vitreous transition temperature (T_g), namely the temperature where an amorphous material changes from vitreous into elastic. At temperatures higher than T_g, the polymer becomes flexible, namely the non-covalent bonds between the macromolecular chains become weak compared to the thermal agitation, the polymer being able to bend and reach high degrees of elongation till reaching the breaking point. In return, under T_g, the molecules are fixed and the polymer is fragile. The acrylic polymers used in painting need a T_g value big enough so that when the film dries it's not tacky (thus prone to attract dust particles from the air) and a value small enough to avoid the craquelures appeared as a result of the polymer's friability. The T_g values of the acrylic polymers vary according to the molecular mass, crystallization degree, heating/cooling speed, structural factors such as tacticity. The only acrylic polymers that possess properties adequate their use in painting are the polybutylene meta-acrylics (pBMA) [2]. According to the value of T_g, the acrylic polymers can be used either as acrylic solutions for painting or as varnishes. Their physical properties are determined by the ratio of the constituent monomers, which by polymerization can produce co-polymers adequate their use in painting. The acrylic polymers used to obtain acrylic emulsions are often co-polymers of the methyl methacrylate (MMA) and ethyl or *n*buthylene acrylate. The value of T_g of these emulsions is approximately 12°C [3]. Another property of the acrylic emulsions which determine the category where the materials will be used is the molecular mass. Dependent on it the acrylic solutions have a certain tack that allows them to be handled easily. An emulsion tack depends on the dispersion medium tack (such as water). Thus, there can be used polymers with molecular masses bigger than 1000000 [2] which have better characteristics regarding the film's endurance after drying.

All acrylic colours dry very fast but there are major differences between the properties of acrylics in form of emulsion and those in form of solution. An acrylic emulsion is characterized by the dispersion of the acrylic polymer in a hydrous solution which makes the drying of the emulsion to occur when the water evaporates which leads to the formation of new bonds in the polymeric chain. Thus, the acrylic emulsion becomes indissoluble after drying making possible to apply successive layers without dissolving the previous layers. However, the acrylic emulsions can be inflated by numerous organic solvents. Besides the surfactants from the composition of the acrylics, they also contain other additives to improve their properties.

On the other hand, the acrylic solutions dry by the evaporation of the solvent and thus can be re-dissolved with turpentine or white spirit. Consequently, it's hard to apply successive layers without solubilizing the previous layers.

POLYVINYL ACETATE-BASED RESINS

Although there are many vinyl resins used in the colours' composition, the most often used is the polyvinyl acetate (PVA) which, like the acrylic emulsions, can be solubilized in water. These are obtained by polymerizing the acrylic resins, keeping their drying mechanism, yet due to the higher value of T_g of approximately 30°C, it forms a hard and brittle film, thus the need to add a softener in the resin's composition. At first, in order to give elasticity to the vinyl resins, diethyl phthalates (DBP) were being added to their composition, later discovering their tendency to separate the film they should have been softening. The result was a brittle and tacky film with a surface prone to dust depositions from the atmosphere. The solution to this problem came in the 60s, when vinyl esters of C_9 and C_{10} [2] were introduced in the composition of the resins. Polyvinyl acetate-based emulsions have inferior properties as opposed to the acrylic ones concerning durability, miscibility and endurance to the environmental conditions but their cost is much below the one of the acrylic emulsions. Most additives from the acrylic emulsions are found in the PVA emulsions as well, but, unlike the acrylic emulsions, they contain polyvinyl alcohols used also as protection colloids.

ALKYD RESINS

The alkyd resins are complex compounds of macromolecular products obtained by condensing aniline with an excess of formaldehyde, in the presence of some acid catalysts that appeared on the market at the beginning of the 1930s. The oil from their composition is necessary to obtain an elastic product usable in painting. Due to the short drying time and increased durability in regard to the oil paints, the alkyd resins have taken the place of oils and natural resins. However, their presence on the market is limited, Winsor & Newton being the only producer of alkyd paints, the other companies introducing alkyd resins in the oil colours' composition. The term 'alkyd' derives from the two main components of the polyester, namely the polyhydric alcohol (polyol) and polybasic carboxylic acid. In order to result in an alkyd usable in painting, the polybasic carboxylic acid must have at least two acid groups ($-CO_2H$), and the polyol to contain at least three hydroxyl groups (-OH). The polyester resulting from these components is usually a hard thermoplastic material, yet by adding a monobasic fatty acid it results in a modified alkyd that can be used as binder in painting. It differs from other polymeric products due to the monobasic fatty acid whose nature determines the alkyd resin's drying time. By adding a saturated fatty acid, it will result in a plasticized material that will not dry and by using a non-saturated fatty acid, the material will have a short drying time.

IMPLICATIONS IN THE CONSERVATION OF MODERN MATERIALS

The conservation of acrylic emulsions has become a subject studied by many conservators and chemists who observed the predisposition of the acrylic pellicles to attract dust particles from the atmosphere, the raised sensibility to temperature variations and the changes induced by organic solvents to acrylic emulsions. The study of Whitmore and Colaluca [3] highlighted the changes of the acrylic pellicles due to accelerated and natural aging. Polymers' addition or condensation decreases the solubility rate of the acrylic emulsions, namely a growing durability of the pellicle to solvents known as 'alteration of thermodynamic solubility'. For example, two acrylic polymers, whose molecular masses differ, will have different solubility moments, not as a result of the different solubility parameters but as a result of the shorter polymeric chains which can break and thus the acrylic polymer becomes soluble faster than the one with longer polymeric chains. In addition to this alteration, the acrylic polymers' pellicles suffer certain yellowing caused by exposure to light. The paint pellicle's yellowing coincides with the solubility decrease and the naturally aged pellicles become indissoluble in benzene two weeks after application, displaying a partial inflation. After 60 days, their solubility can be made only at very high temperatures.

The additives or the residues from the polymers' synthesis can become catalysts in the process of acrylic pellicles' decoloration. The accidental addition or generation of these catalysts may be the cause of excessive decoloration of acrylic products applied in art. The chromatic alteration may also be attributed to the nature of the polymer/polymers from the acrylic emulsion, identifying chains (C=C-C=O) that can initiate processes of decoloration of the polyvinyl chloride. Light absorption at 215 nm [3] wavelengths of the UV spectrum can be a consequence of the presence of the types of polymeric chains mentioned above. Thus, it can be justified the decoloration occurred due to prolonged exposure to these wavelengths of the UV spectrum.

The pigments in acrylic emulsions tend to stabilize the binder useful in absorbing UV radiation. Mineral pigments have a better resistance than the organic ones, the titanium dioxide being the most appropriate in this regard. Of the two crystalline forms, the natural titanium oxide (rutile) [4] exposed to the outside is not deteriorated by UV radiation. Anatase, the other crystalline form of the titanium oxide, has a high reactivity to the UV light and can form radicals resulting in the degradation of the polymer.

The properties of a dry acrylic pellicle differ substantially from those of an oil film, hence the treatments commonly used for traditional painting are not recommended for the conservation of modern and contemporary paintings. The biggest problem is the increased sensitivity of synthetic resins to organic solvents often used for the cleaning of traditional paintings.

Acrylic colours' affinity to attract dust particles from the atmosphere can be attributed to the following factors:

1. the vitreous transition temperature, molecular mass, pellicle forming temperature. If all these values are low, then the pellicle will be soft and tacky at room temperature, which makes it prone to dust accumulations.
2. electrostatic charging. Acrylic films are not conductive and thus can be loaded with static electricity attracting dust particles from the air.

3. pigment. Depending on the amount of pigment used in the acrylic emulsions, it may act as a barrier to dust deposits, but the use of large quantities of pigment will also lead to an irregular surface and hence a mechanical anchoring of the particles in the atmosphere.
4. hydrophilic additives (surfactants). The additives from the surface can attract dust.

Acrylic emulsions' sensitivity to organic solvents limits the conservator's options for cleaning the colour layers and varnishes. Removing dust deposits becomes difficult when the aim is preserving the surface texture, gloss and colour. Using a solvent with a polarity higher than that of white spirit's leads to inflation and partial solubilization of the acrylic paint. Although most acrylics are not soluble in white spirit or water, the additives from their composition may be dissolved by these solvents. This becomes a problem when the paintings made in acrylic need cleaning of various types of deposits or removing traces of vandalism. Mechanical cleaning using gums, for example Staedler Mars, Plastic 52650 (grated), Groom/Stick and Dry-Cleaning Sponge [5] is often used before testing with wet cleaning methods.

The gloss, brightness and results of visual examination conducted by Saulnier are strongly influenced by various parameters such as non-absorbent surface of the support, the presence of dust and micro-climatic conditions. The non-absorbent nature of the substrate increased the migration of the additives towards the surface of the film. Visually, it has been noticed an increased glossiness of the additives as opposed to the polymer's, and they were more easily removed or scattered on the polymer' surface during cleaning. Dust particles from the atmosphere were absorbed preferentially by these additives from the acrylic surface film. During the dry cleaning process, the additives were removed totally or partially depending on the environment conditions in which the tests were made. In general, low temperatures and values of R.H. strengthened or dehydrated the additives, fixing them on the polymer' surface. Following the experiment conducted by Sauliner on testing dry cleaning methods using five types of gums, it was recommended the use of the gum Staedler Maers Plastic 52650 to remove the deposits from the surface of acrylic pellicles without changing the physical and aesthetical properties of the acrylics such as gloss and brightness.

Even water or the hydrous solutions may have a negative effect on the acrylic films that may remain soluble in water more than a week from the time of application. After drying, they start to become insoluble in water, but the conservators often encountered the problem of the acrylic film inflating in the presence of water. Murray's study [6] showed that the cleaning treatments using water as solvent affect the acrylic pellicle by diminishing its mechanical properties and the dimensional changes. Depending on the method chosen in Murray' study, by total immersion in a hydrous solution for one minute or one hour, certain differences were noticed which surprisingly had better results when longer immersed. The samples immersed for one minute resulted in a decrease of mechanical strength unlike the ones immersed for one hour. This can be explained by the limited penetration of the hydrous solution within a minute, allowing the cleaning solution to penetrate only the upper layer of the acrylic colour producing tension forces due to the inflation of the surface. On the other hand, during the one hour immersion, the solution penetrated the entire sample reacting with all its components, thus reducing the tension forces within the material. After drying, the sample immersed for one minute increased in volume as opposed to the sample immersed for one hour that returned to its original size. Immersion, even if it is not a cleaning method, has been chosen as a means of dissemination of the effects that may be produced by repeated cleaning on the paintings.

Although they appeared mid-nineteenth century for commercial purposes, plastics began to be used as painting material by artists of the 20th century. Right from the introduction of the acrylics there were numerous discussions regarding the behavior of these new materials in time. Knowing the composition and the changes in time of the additives in acrylic colours and the multidisciplinary collaboration represent the first steps in developing new adequate methodologies for the conservation of modern art works.

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