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Research Article

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Optimizing catalytic drying of paints and varnishes: Case study at Smalto

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ABSTRACT

This article reports on the study of a mixture of catalysts used on the drying of paints and varnishes at the Smalto Paint and Varnishes Production Unit in Douala, Cameroon. Drying of paints and varnishes depends on several factors including the environmental conditions. While the chemical composition of the paints vary widely, it is inconceivable that the manufacturers can specify with accuracy the conditions for optimizing the drying of the various products in different environments. On receiving a new alkydresin the company requested our services to study its optimal drying time. We therefore examined the different raw materials that go into the compositions of paints and varnishes, their different production methods and ways and means employed in drying the paints and varnishes. In order to arrive at an appropriate mixture of catalysts for an optimal drying time, three different organometallic compounds (lead, cobalt and calcium naphthenates) were tested severally and in mixtures until an appropriate mixture of 2% catalyst was arrived at that gave a minimum drying time of 1.57 hours. Mixtures of catalysts below and above this combination gave higher drying times reaching values beyond twelve hours, same as for non-catalyzed drying. The appropriateness of the dried paints and varnishes were tested experimentally using standard equipment.

Keywords: Catalysts, Optimization, Drying time, Resins.

INTRODUCTION

Paint and varnishes are liquids or powders consisting of the following constituents: binder(s) or resin(s), solvent(s), additives and eventually, pigment(s) andfillers. They are used to cover surfaces in an artistic and decorative purpose or protection of support. Over time, there has been awareness of the need to protect the environment and as such new formulations have been put in place that are less rich in solvents, less polluting, such as paints with high levels of dry extracts which can be cross-linked under the influence of ultraviolet light or by electron bombardment. Paints or varnishes once applied on the dry surface can spread thinly on various media forming by evaporation of solvent, an adhering film which is resistant, opaque, white or coloured. Drying can be done physically by simple evaporation of solvent or by a chemical reaction (polymerization) or a mixed process combining the two. In systems that implement drying by a chemical process, catalysts driers or accelerators are generally used and this reduces as much as possible interval between painting and object being available for use. A glaze differs from a paint by virtue of the transparency of its film that does not mask the support but which can be coloured with a soluble dye in the middle and not a pigment.[1] The first known examples of pictorial representations date back to the Magdalenian, the parietal from the caves of Lascaux in France are among the most famous. In Asiaas early as the 6th millennium B.C., there is found evidence of the use of pigments extracted ores, preparations, and organic components. Indigo pigment extracted from the Indigo plant was already used in ancient Egypt. Gum Arabic, egg white, gelatine and natural wax were first binders of these pigments. In China, as early as the 2nd century B. C., lacquers were used in architecture. Linseed oil was used by artists from the 15th century. Synthetic binders were marketed for the first time in1907. White lead and white lead pigments were widely used in the 17th century, as well as lime diluted to cover the walls of houses. Titanium dioxide industrial marketing began in 1919.[2]

The main areas covered by the coating products are building, automotive industry, the timber industry and the fight against corrosion. Germany, leading European producer of coating products, had in 1998 some 300 manufacturers of paint, with 23,000 employees and generated more than 1.7 million tons of paint, varnish and thinner, with a total value of approximately EUR 4 billion, or about 0.7% of GDP.[3] Our work will consist first a review of the various raw materials used in the manufacture of paints and varnishes, then in a second step to study experimentally analkyd resinin order to determine the optimization conditions for of drying paints and varnishes where it could be used as a binder.

Theory

It is necessary to classify paints in groups because of their diversity. This classification can be based on composition and their uses.

1-1Classification by use

The paints sold in the Cameroonian market can be classified as decorative or industrial. Decorative paints are used in homes and are applied on interior and exterior surfaces. The binders used in them are diverse, being principally of synthetic polymers (alkyd and acrylic resins, etc). The binders give a good cover and are resistant to alkali attack present on block or plastered surfaces. Industrial paints are those used in equipment which is subjected to high pressures and speeds like on automobiles, limit corrosion of metals like in marine paints used on ships, boats and oil rig platforms. The main binders in industrial paints are special acrylic polymers, polyurethane resins resistant to abrasion, lead paints that slow or stop corrosion, polymers hardened by ultraviolet rays andepoxy resins.

1-2Classification by composition

1-2-1Solvent paints

These are paints using solvents other than water. The ensemble of solid materials are called dry extracts, which is what remains after the drying out of the volatile components of the paint and this volatile component cause pollution of the environment.[3]

1-2-2Water paints

The troubles and dangers (dizziness, headache, risk of cancer, etc) that solvents cause in the making of paints caused formulators to replace these organic solvents by water. Basically, these paintings are solutions or dispersions or emulsions of the binder in water. As for solvent-based paints, binders are classic resins i.e. natural polyesters or polyesters modified by fatty acids, acrylic resins, epoxy esters and phenolic resins. These resins are grafted polar, more often as carboxylic groups giving an acid index value between 40 and 70, but also of the hydroxyl groups or amino acid, giving products which after neutralization have pH>8 and water soluble. Few binders are soluble in water but they are fitted with load-bearing side chains of acidic or basic functional groups which once neutralized make the binder soluble in water. The products of neutralization, amine or acid, evaporate after the application of the paint and the film that forms is more soluble in water. The protection of the environment, in this type of paint is good in relation to the air pollution due to the non-toxicity of water.[1]

1-2-3Powder Coatings

A powdercoating is composed of one or more resins, pigments, a hardener and occasionally fillers. It contains no solvent. Depending on the nature of the resin, there are two families: thermosets and thermoplastics. Thermosetting powders are by far the most commonly used because of their low cost and they are applied by electrostatic powder coating which results in very thin layers being obtained. The principle of powdering is to deposit the powder with a mean particle size of 30 to 50 micron on the substrate andby baking subwoofer, to produce first sticky particles and curing them to get a smooth and homogeneous film. The subwoofer is made in a convective oven where there is the advantage of uniformity of temperature, or in an infrared oven where the fusion can be better separated from the polymerization. Resins used are epoxy resins hardened with dicyandiamine for example, pure carboxylated polyesters hardened with triglycidylisocyanurate and polyurethane hardened with a cycloaliphatic or cycloaromaticisocyanate.[4]

2 Raw materials

2-1Binders

Binders are film-forming materials, generally organic in nature. For the chemist, these are polymers or oligomers or oligomers that polymerize during the drying of the paint. The role of the binder is to link the other elements of the formulation by forming on drying a film adherent on a given substrate. Binders are therefore essential raw materials in the composition of a coating according to their origin and are distinguished as natural and/or synthetic.

2-1-1 Natural Binders

Natural binders include natural resins (colophane, cellulose derivatives, natural rubber) drying-oils (castor oil, soya, linseed, wood from China, fish etc.). Bitumen and pitch are less and less used in paints and varnishes in the raw state because they present a good number of unwanted properties. For examplerosinewhich is a natural resin that is still used today, with abietic acid as main component, cannot resists oxidation and turns yellow because of its reactive double bonds, its acid index is high, solubility and compatibility with other components of the paint is problematic. Its molar mass is low unlike natural rubber which suffers from a high molar mass. Natural binders are used today mainly in a modified form with changes made to improve the quality of these resins.

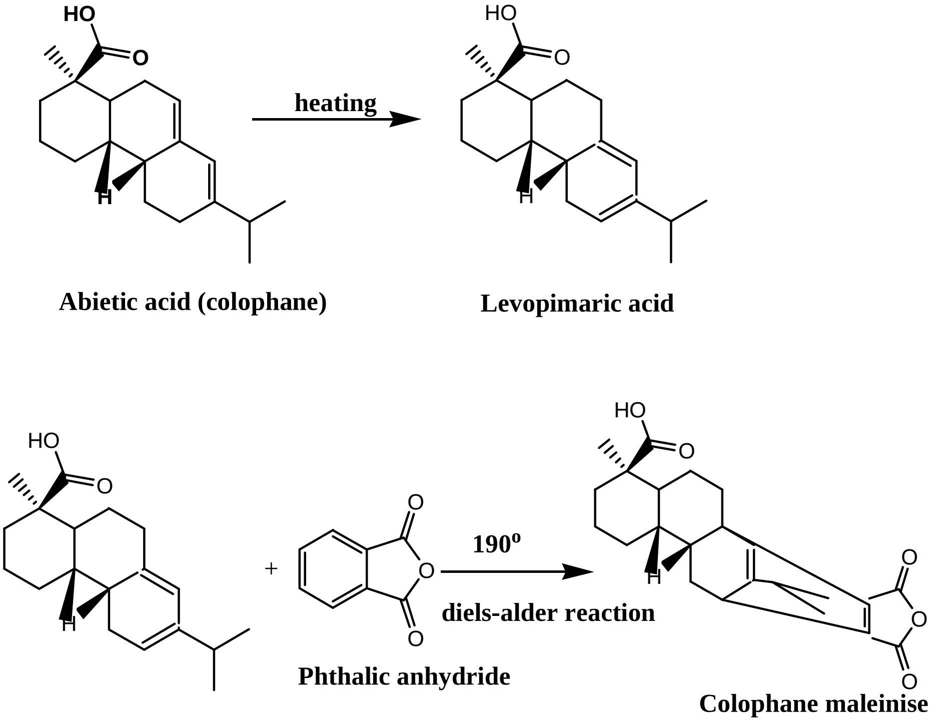

Figure 1 shows a reaction that modified resin to reduce its double bond reactive content and produced unsaturated dicarboxylic acids or anhydrides.[5]

2-1-2 Synthetic Binders

This is a large family with the main members being: a) saturated polyesters which are obtained through esterification of polyols having at least 2 functional alcohols, acids or (especially bi-functional) multifunctional organic anhydrides, aliphatic, saturated, cycloaliphatic or aromatic. Relatively soft, long chain, linear polyester or little branched and can be physically dried. They are associated with very hard binders; b) unsaturated polyesters which are obtained through esterification of diols by a mixture of maleic anhydride and other anhydrides or dicarbolic acids. These polyesters are used in the varnishing of woodwork and furniture and also enter the composition of paints for the automotive industry. c) alkyd resins which are polyesters modified with oil or fatty acidbase or synthesized organic acid of high molecular weight.Figure 2 is the reaction with an alkyd resin, composed only of oil glycerol andortho-phthalic acid. There are short alkyds resins in oil (less than 40%), medium oil alkyds (between 40 and 60%) and long oilalkyds(between 70 and 85%). The oil content of the long alkyd oil brings a good tension in the films, great flexibility and ease of implementation. Medium oil alkyds are used primarily in industrial paints intended for machines, utility vehicles, household equipment, etc.[8] d) Acrylic resins or poly-acrylates are mostly prepared in liquidform, from acrylic monomers by radical polymerization in solution. They are used as binder or as a complement binder in paints formulated to dry by evaporation of the solvents and intended for applications on virtually all substrates. Their main features are resistance to water and alkaline products, flexibility, good grip and, in the absence of styrene, resistance to yellowing and a better stability of brilliance against the aggression of ultraviolet rays.[9]e) The essential feature of epoxy resins is the presence of a triangular ring formed by two carbon atoms and one oxygen atom that is calledthe epoxy group. Theyshow excellent resistance to chemicals, high flexibility, adhesion unto metals and other substrates, but they fade and turn yellow when exposed to sunlight.[10] f) A urethane is obtained by reaction of an isocyanate with alcohol. Polyurethanes resins have properties such as flexibility, tenacity, universal adhesion, resistance to chemicals, water and yellowing when exposed to weather.

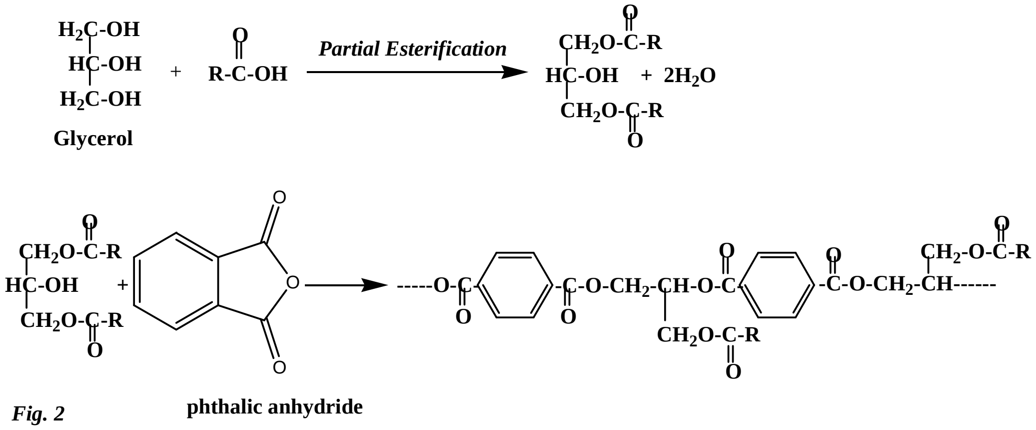

Fig. 2

2-2The Solvents

A solvent is a simple liquid or mixture, volatile, having the property of totally dissolving a given binder. This definition applies to true solvents in opposition to latent solvents which do not directly dissolve binders but will accommodate them in the presence of true solvents.A thinner which is a simple volatile liquid, or a mixture, which without being a solvent, can be used with a solvent until a certain threshold called dilution ratiowithout adverse effects such as the precipitation of the binder.[11]The most important role of the solvents in paint products is the point of viscosity for the application and regulation of this viscosity during the drying process. But the solvents still exert their influence at different stages of manufacture, the application and drying of paints as shown in the following examples:

- The action of solvents exerted on the factors that determine the speed of wetting of pigments, such as viscosity of the binder solution and interfacial tension between the solution of binder and pigment surface. Solvents are in competition with the binder and dispersion agents to be absorbed at the surface of pigment particles. The nature and strength of the interactions between the binder or solvent on the one hand and the surface of the pigment on the other hand, depend therefore on the nature of the pigment, the parameters of solubility of solvent and the binder or solvent hydrogen bonds.[11]
- When a true solvent is the last component of a solvent mixture to leave a film, the brilliance of the film is better, as it is decisive on the surface coating. Real solvents of high boiling point permit the different components of the film allow consistentbonding during drying, asthere is sufficient fluidity to facilitate the departure of the solvent with a minimum of ramous and leave the surface of the film smooth and flat.
- Solvents can have a certain influence on the mechanical properties of the paint film. A more or less large solvent power allows the solvent, either disperse the molecules of the binder or arrange them in a certain order. Some solvents are capable of reacting with specific binders and thus reduce the cross-link density that corresponds to a relaxation of the binder. But if solvent remains imprisoned in the paint film, it goes dry and remains soft and sticky.

2-3Pigments and Extenders

Pigments are generally substances in form of fine insoluble particles used in a dispersed medium because of their optical, protective or decorative properties. Chemically, pigments are in two categories, organic nature or metallic. Organic pigments are generally classified in function of their composition in three groups: azo, polycyclic and metal complex pigments. Copper phthalocyanines are the main representative of the pigments of metal complexes. Cu - Pc cover a range of tones ranging from yellowish green to reddish blue, their hue is function of the degree of halogenation. By replacing in each 14-16 atoms of hydrogen molecule by chlorine, it gets green pigments, if chlorine is replaced by bromine (between 8-13 atoms), the tint will be even more yellowish that the number of bromine atoms are high. Mineral pigments are grouped by colours (red, yellow, green, blue, etc) on the one hand and also by chemical nature. In the second case are oxides and oxy-hydroxides (iron, chromium oxides, etc) and pigments of bismuth, cadmium, cerium, chromates and ultramarine blue.[13]The power of colouring in pigments lies on selective light absorption. The essential cause of the absorption of light resides in a change in the electronic state of the absorbing substance.White pigments are usually inorganic oxides like titanium dioxide TiO_2 that is most employed, antimony oxide (Sb_2O_3) and zinc oxide (ZnO). Other insoluble inorganic white components also used are: zinc sulphide (ZnS), white lead ($2PbCO_3.Pb(OH)$, lithopone ($ZnS + BaSO_4$). Red, yellow, black or brown iron (Fe_2O_3) oxide, green chromium oxide (Cr_2O_3), red lead oxide (Pb_3O_4) are other inorganic oxide pigments. Lead, zinc, strontium and nickel chromates shades offer variety of yellow and orange.[2]Pigments are further classified according to their aesthetic properties; black, white, luminescence, coloured and brilliant. Hence, these differ from dyes because the latter are soluble in the medium of usage. Extenders are grainy or powdery in form being insoluble and are used in paints to modify certain physical properties.[12]They are natural or synthetic, usually white or yellowish in colour depending on function of the included impurities. The role of extenders in the coating products is generally to modify the rheological properties (e.g. viscosity), reduce the brilliance (silica), increase the mechanical properties such as resistance to abrasion, as is the role for example of talc and finally reducing the cost of the paint by adding calcium carbonate. The most common jobs for extenders are as primary paints, mastics primers, emulsion paints and plasters made from synthetic resins. Their employment in glossy finish paints is limited.[14]

2-4Additifs

These are substances which are added in small quantities in paint products. Additives used in coating products are many and may include:

- Anti-foaming agents (Dimethlypolysiloxanes, polyacrylates, siliconfluorides)
- Surface tension reducing agents (silicons, modifiedsiloxanes)
- Wetting and dispersing agents (polyphosphates, polyacrylates)
- Rheological agents (derivatives of cellulose, bentonite, hectorite)
- Corrosion inhibitors (lead pigments)
- Drying catalysts (Co, Mn, Pb, Zn, Ca, etc.)
- Biocides agents (2-hydroxybenzophenone, 2-hydroxyphenylbenzotriazole, formaldehyde, isothiazolinone, chlorocetamide).
- Light protecting agents that absorb ultraviolet rays and these are in four groups: 2-hydroxy-benzophenone, 2-hydroxyphenyltriazine oxalanilide and 2-hydroxyphenylbenzotriazole.

1-3Manufacture of paints and varnishes

The manufacture of paints assumes strict respect of a series of systematic procedures that can be structured in several successive stages:

- Reception and storage of materials in a mill.
- Weighing and introduction of materials first into the disposer.
- Follow-up control grinding of the fineness of the sample using a Hegman gauge.
- New round of grinding for stabilizer dispersion.
- The grinding elements are separated from grinding paste by filtering on coarse-mesh sieve. The dispersion is pumped into the mixing vessel.
- Introduction of other additives and stirring to homogeneity.
- Staining of the product by the colourists and sampling to evaluate the colours and analyse the film viscosity.
- Ultimate verification of viscosity, density, GE and pH. Inclusion of solvent and drying.
- Sieving and filtering the mixture before pouring into jars.
- Labelling and filtering the mixture before pouring into jars.
- Storage of the finished product in warehouse.

In preparation of varnishes, steps four and five are skipped.

1-4 Drying of paints

There are three modes by which paints get dried; physical, chemical and a mixture of the two. In the first mode, the binder molecules undergo no chemical process during drying. The transition from the solid state to the liquid state is determined by a physical phenomenon: evaporation of the solvents for binders in solution and coalescence for emulsion binders. Sustained speed of drying influences several parameters. At the beginning the evaporation is influenced by the pressure of steam over the film, but also interactions between molecules of solvent and binder, ventilation and the glass transition temperature T_g. If the T_g is much lower than the drying temperature, the rate of diffusion of solvent in the film exceeds the rate of evaporation. In a contrary situation, the viscosity of the film will be so high during the drying that the solvent will not diffuse quickly to the surface of the film in order to evaporate. Here is a factor limiting the speed of drying and to get total evaporation of the solvent, the temperature of the film has to be higher than T_g.[3] In the course of coalescing, the polymer particles move closer when some water contained in the paint coating evaporates. When particles are touching, the small space that separates them and contains water behaves like a capillary. The capillaries forces deform the particles pulling more and more to each other. As the capillaries become closer, they ensurelarger forces. Under pressure thus obtained, the phase liquid is expelled out of the film and finally, polymers particles weld between them.[3]

In the process of chemical drying, binder molecules undergo chemical transformation called polymerization, in which one or several monomer molecules are trans-formed into a substance composed of long interconnected or network of three-dimensional macromolecules. There is polymeriza-tion by oxidation also called siccativation, polycondensation, polyaddition and radical polymerization.[1]

Siccativation is the process of hardening in the presence of oxygen in air of binders containing unsaturated fatty acids such as siccative oils, alkyds, alkyd-urethanes and epoxydic esters. There is fixation of oxygen at the unsaturatedsite present in the molecules of the binder with formation of hydro-peroxides which create covalent bonds between themacromoleculesof the binder in accordance with the following mechanism:

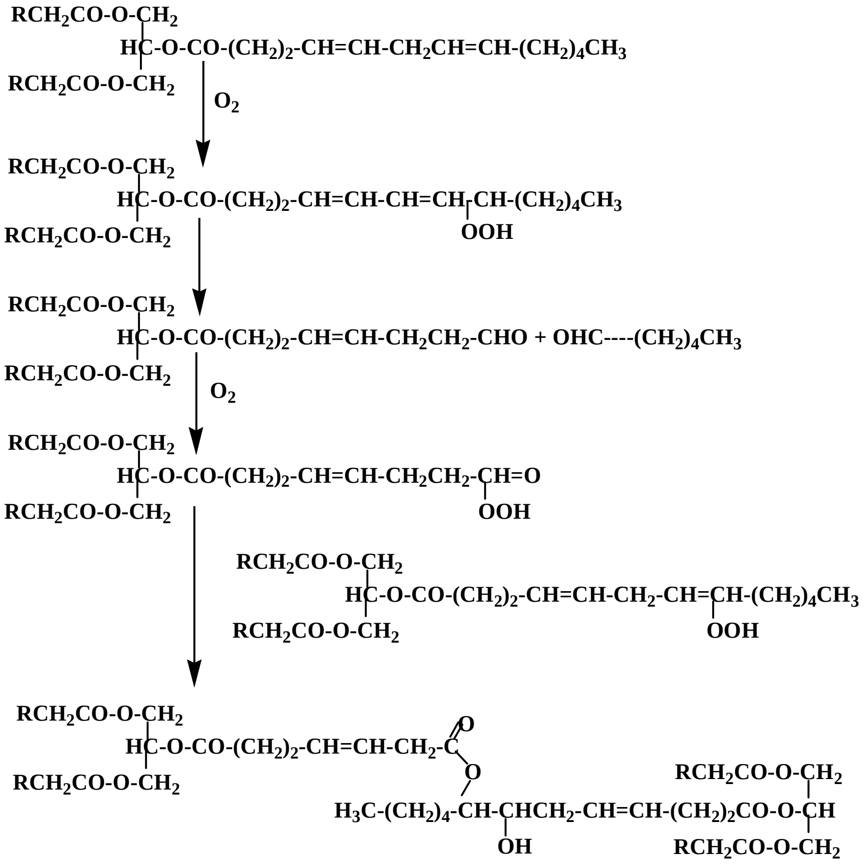

Figure 3: An unsaturated ester reaction on siccativation

It is a slow-drying process that requires no outside energy input but the presence of a catalyst (salt of cobalt, lead, calcium etc), to reduce the drying time.

- **Polycondensation**

Under the action of heat and a catalyst, poly-condensation translates into the creation of a covalentbond, with elimination of a small molecule such as water, alcohol or formalin, between two reactive groups of two different macromolecular chains. The drying speed is fast and once the film is hardened, the poly-condensation reaction stopsand does not interfere with the ageingof the film.Poly-condensation reactions are numerous:there can be esterification between a hydroxyl andCarbonylcompound, for example of polyesters or of thermosetting acrylicscompounds;esterification between a hydroxyl and possibly hydroxymethylcompoundin the case of aminoplastic and mouldings, and elimination of a molecule of formaldehyde starting with two hydroxymethylated or ethergroups.

- **Polyaddition**

Polyaddition results in the formation of certain functional groups that can react at room temperature with compounds with labile hydrogen. They create covalent bonds without elimination of small molecules like between epoxides and isocyanate groups. The speed of the reaction which is fast at room temperature is a function of the structure of compounds involved and the presence of catalyst.

- **Radical Polymerization**

The radical polymerization process applies to the resins such as unsaturated polyesters and acrylics. In the presence of photo-initiated radicals in the UV range or from electron bombardment, the monomer molecules are transformed into active molecules and their reactions last fractions of a second or few seconds.

In mixed drying, any of the chemical methods explained above can occur plus a physical process such as employing high temperature for fusion of powder paints or paints used in furnaces.

Siccatives

Siccativesare chemical substances that promote hardening of drying oils or resins dried through oxidation. They are generally sold in the form of stable dispersions in organic solvents. They are distributed fully and evenly in the mass of the binder because of their 'oleosolubility'. Organic chemistry offers an important choice 'carriers' responsible for their oleosolubilite. These are for example, alkyoxides, organometallics, esters soaps and many complexes that are metallic salts of natural or synthetic organic acids having between 8 to 11 carbon atoms. This last group is the most used due to their efficiency, availability and price. Metals include: cobalt, lead, manganese, zinc, cadmium, magnesium, barium, cadmium, iron, zirconium, cerium, Tin, copper, aluminium, vanadium, nickel not to forget mercury, strontium, chromium, bismuth, titanium.[15]

Primary siccatives consist of versatile metal soaps and are involved in varying degrees in the process of polymerization and binders that are dried by oxidation. The most common are cobalt, manganese, and lead. Their passage under the influence of oxygen of the airand their less than stable lower or higher valence mostly explains their operation.Auxiliary driers do not intervene in the polymerization process. They however promote by their presence the action of primary driers with respect to which they are sometimes intended for a certain synergy. The most common are calcium and barium soaps which are excellent dispersantsandwetter of surfaces and zinc soaps which in addition have low surface tensionto hold film permeable to air during drying. The coordination driers intervene almost only in the polymerization process. The latter action is independent of the absorbed oxygen. They provide essentially their mobility in the binder. These are metals such as zirconium soaps which by their coordinating valence form complexes with certain reactive groups of the binder and participate in cross-linking. Besides the acceleration of drying time, driers are used also to influence to some extent the characteristics of the film, namely, colour retention, hardness, and flexibility. These secondary performance require the use of a combination of metals.[15]

Calcium soaps do not participate in the process of autoxidation. They perform synergy manifested on the action of cobalt and manganese, thanks to these excellent wetting and dispersing properties. Calcium soaps still tend to decrease the viscosity of paint or even destroy the thixotropic gels. Calcium contributes to the formation of a harder film. It prevents, in large part, the precipitation of lead phthalate attributable to free phthalic acid in alkyd resins. Combinations of cobalt, lead, and calcium are the most widespread and generally lead to good drying time.The oxidative activity of lead is significantly lower than that of cobalt and manganese. Its influence on the process of destruction of hydro-peroxides is limited. It is in the phase of polymerization that its intervention is decisive. Lead soaps work in the deeper layers of the film. The resulting film is of remarkable hardness. The harmful features of the derivatives of lead require the observance of safety precautions during the work of painting or maintenance of painted works. Cobalt soaps are catalysts of oxidation by excellence. Indeed the cobalt easily passes the bivalent to trivalent state and is essential during the first phase of autoxidation, including the formation of hydroperoxides. It has been shown experimentally that cobalt siccatives give rise to the greater absorption of oxygen. The rapid oxidation of cobalt siccatives with binders result significantly in increase of the surface film, and this very tight film surface prevents the introduction of oxygen at the base. The film thus remains soft and flexible; with intense training ride. For a determined degree of humidity, the drying time varies in the opposite direction of the temperature. Effects due to the humidity of the air significantly vary as function of the temperature though it is not possible to draw strict rules. However, high humidity air upsets drying even at high temperatures (tropical climate). Solar radiation increases the rate of drying particularly light of short wavelength (blue, violet and ultraviolet)

EXPERIMENTAL SECTION

MATERIALS

The opportunity which has guided our work was the arrival in the laboratory of Smalto, a sample of resin intended to replace another that did not give satisfactory outcome. However, as is often the case for certain resins, the technical specifications for the supplier did not give driers percentages to be used to accelerate the drying of this resin. For this reason, we have conducted a number of tests to achieve this end. It's a long alkyd resin in oil, modified by soybean oil whose main fatty acid is linoleic acid. It consists of 24% of phthalicanhydride and 63% soybean oil. The technical specification indicates that the resin is soluble in white spirit, xylene, methylethylcetoxine and butyl acetate with a pH between 6 and 10, its viscosity between 7 and 8 poises and its dry extract between 69% and 71% phthalic anhydride and soybean respectively. White spirit was used as solvent, its role being to adjust the viscosity of the film-forming material. When the binder is very viscous it becomes difficult to handle.Three metals were used as siccatives: lead, calcium and cobalt; their main role being as catalysts. Methylethylcetoxine was used as additive its function being to render homogeneous the reaction medium. The assays have been made from the reference formulation contained in table 1,the mass composition of the mixture of driers we have prepared is given by table 2. The driers used are not pure but salts of naphtaotes in solution of white spirit.

- A Beckoller (with six needles) records the drying time; allowing us to measure the length of the successive stages by which a layer of paint or varnish passes, drying by oxidation andthicknessformed when applied on a glass plate. The speed of fine needles displacement is constant on the surface of the freshly applied film drawing furrows whose appearance change over time. Each stage of drying has a characteristic profile and this feature can be measuredto give the duration of drying. The NFT 30-037 standard defines the steps as: a) drying without absorbing dust from atmosphere; b) dry on touching and c) dry to withstand normal usage conditions.
- Thermohygrometer measures both temperature and humidity of air.
- Application instrument with 30µm and 60 µm opening.
- Etuvescaltec: It's a mini camera combing a scale and a heating system whose temperature rises to130ºC. This electronic device allows the determination in a few minutes the percentage of the solid residue that remains after evaporation of volatile matter. The measurement is performed on a mass of 1 to 2 g fresh varnish or paint.

METHOD

Weigh a mass of 72.1 g of resin (dry extract = 74.13%). Place in a 300 ml miniature reactor. Add 27.1 g white spirit, 0.5 gmethylethylcetoxine and 0.2 g mixture of siccatives. Using a spatula, the mixture is stirred vigorously until homogeneous mixture is formed. Leave stand for a few minutes. Using an applicator, place a layer of 60µm thickness on alabelled glass plate. Place the glass plate on drying apparatus. Adjust the needle of the Beckoller on the plate, scale the time to twelve hours and activate. Repeat the experiment by varying the percentage of the main driers (siccatives) and solvent in a way that the mass of the prepared sample stays constant at 100 g. with the mass of the other components remaining constant.

RESULTS AND DISCUSSION

Autoxidation is a non-induced chain reaction consisting of the more or less rapid fixing of oxygen on an organic or inorganic substance in the presence of radical initiator.[9] Alkyd resins modified by drying-oils have this property of spontaneously fixing oxygen from the air at room temperature. The fundamental cause of autoxidation is the structure in the oxygen radical: each oxygen molecule has two relatively energy-rich single electrons, with which it is able to attack certain sensitive substances. In this experiment, soybean oil in alkyd resin is a semi-siccative oil (iodine index 127) non-conjugate whose percentage of the main fatty acid (linoleic acid) is 54%. The attack of the oxygen first forms hydroperoxides, which then decompose to form reticulate polymerization. In experiment no. 1 (table 3)the resin is dried without catalyst. The observed drying time is greater than 12 hours, a finding that was predictable. Indeed the non-conjugated double oils dry slower than combined oils. This difference is explained by the fact that the polymerization of conjugated oils are progressing especially after formation of C-C bonds, without prior formation of hydroperoxides.[9]Drying time in experiment no. 2 remains higher than 12 hours despite the presence of calcium. This shows that calcium does not intervene in the process of decomposition of hydroperoxides; its advantage rest in wetting and mechanical properties. The presence of only lead in the third experiment shows a drying time of 7 hours but with a remaining surface film that is soft. The lead therefore participates in the decomposition process of hydroperoxides but not as effectively as cobalt. Indeed, using only cobalt in the fourth experiment reduces the drying time to six hours. The difference between the two indicates that lead reacts in depth, while cobalt reacts on the surface. The film obtained in experiment no. 4 has a wrinkled surface. Given the preceding, it can be noted that the use of a unique catalyst does not give satisfactory results. Indeed, the desired drying time must be less than 2 hours andwith this in mind; the series of experiments that follow (no. 5 to 20) are implemented by using the combination of the three catalysts (Co + Ca + Pb). Figure 4shows that in general, the drying time of the resin containing catalyst mixture decreases significantly when the amount of catalyst increases up a minimum drying time of 1.57 hours (2% catalyst) after which the drying time starts to grow despite the increase in the amount of catalyst.The rise of the drying time despite the increase of the quantity of catalyst is explained by the fact that: the more the amount of catalyst increased drying on the surface of the film so fast that it prevents oxygen of the air from penetrating into deeper layers of the film. Indeed at this point, we found an intense formation of wrinkles on the film surface during the experiment. The contribution of catalysts significantly reduces the drying time of paints and varnishes dried in air by autoxidation. However, it must be put into perspective. The time of drying of this type of product is slow when compared to that of paints and varnishes dried through subwoofer in the oven or under the effect of ultraviolet radiation that lasts only a few seconds.

Table 1

Reactants	**Weights (g**
Resin alkyd	72.1
Catalyst mixture(Co, Ca, Pb)	1.7
Methylethyl-cetoxime	0.5
White spirit	25.7
Total	100

Table 2

Siccatives	**Weight %**
Lead	33.9
Cobalt	16.5
Calcium	49.6
Total	100

Table 3: Drying experimental results from Smalto

Sample	**Resin (g)**	**Siccative (%)**	**Methylethyl-cetoxime (g)**	**White spirit (g)**	**Total (g)**	**Drying time (hrs)**
Nº. 1	72.1	0	0.5	27.4	100	>12
Nº. 2	72.1	Calcium=1.7	0.5	25.2	100	>12
Nº. 3	72.1	Lead = 1.7	0.5	25.2	100	7
Nº. 4	72.1	Cobalt = 1.7	0.5	25.2	100	6

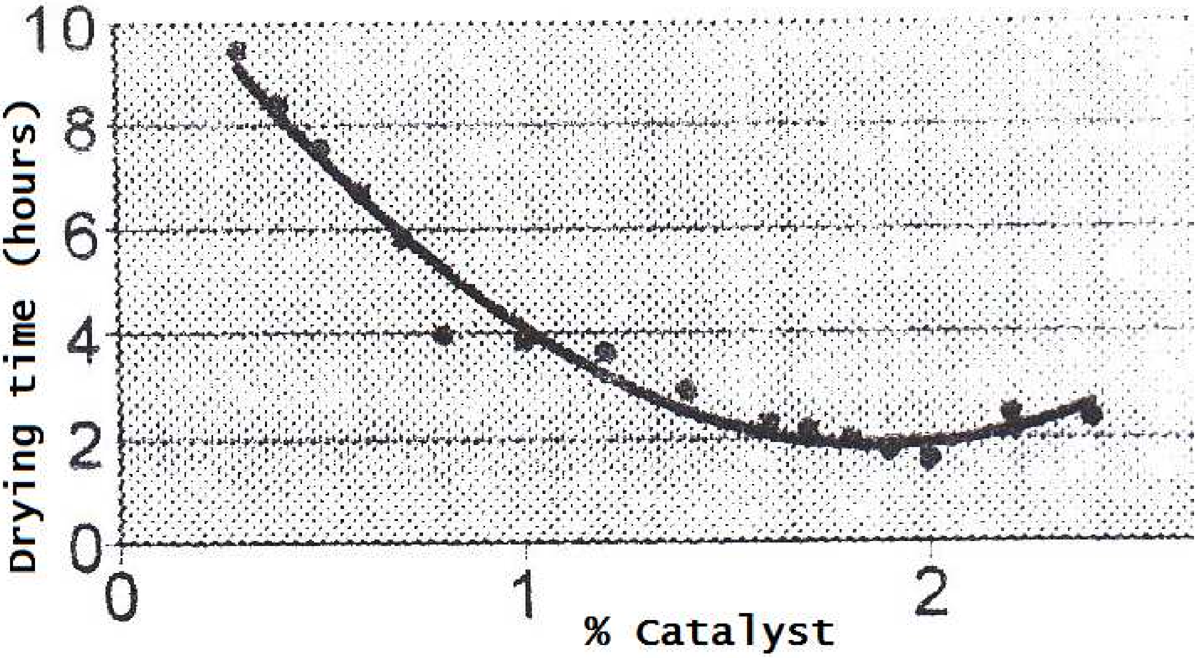

Fig: 4 Drying time versus catalyst concentration

CONCLUSION

The initial task was to study the evolution of time is drying alkyd resin modified by soybean oil and catalysed by a combination of driers (siccatives) called catalysts. At the end of this work we can draw the following conclusions: the siccative-free resin dries very slowly. The speed of drying of resin studied when catalysed by calcium is as good as when not catalysed. However when the resin drying is catalysed either by cobalt or lead, there is a significant evolution of the drying rate but the drying time is still quite high. This does not permit the use of only one of these catalysts. The speed of drying of resin catalysed by the combination of the three catalysts increases rapidly as the percentage of the combination increases up to a breaking point after which there is a decrease of drying rate.Our work has focused on a single combination of the mixture of the three driers. Further trials should be conducted in the future with several other combinations of the three driers in order to determine which allows to obtain an optimum drying time and form a hard film able to withstand wear and tear of daily use since the driers have very slow kinetics once the film hardens and what causes ageing of the film with loss of flexibility and decrease of the brilliance. The siccative whose first role was to accelerate the drying rate, continuing its action also in this was in this stage of aging. On the other hand, it will be of great interest for the maker of the coating to research products that will replace lead by another metal playing the same role as the zirconium. In effect the handling of lead represents a potential danger for the health of man because of its cacogenic nature.

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