INSTITUTO SUPERIOR DE ENGENHARIA DO PORTO
MESTRADO EM ENGENHARIA QUÍMICA

Functional coating for industrial cork applications.

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“Thinking should become your capital asset no matter whatever ups and downs you come across in your life”
APJ Abdul Kalam

Thanks

The great journey that has gone through so many years, those full of adventures and pre-shrines, culminating with a present of work, could hardly be exclusively with my will and want. And so, I would like to thank people who, in one way or another, have contributed to this goal.

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RESUMO:

A cortiça é cada vez mais utilizada como material de construção. Quando se utiliza cortiça na construção civil, é comum protegê-la com tintas e vernizes. No entanto, a cortiça é um material que traz alguns problemas: libertação de taninos que mancham tintas de cor clara, tem tendência a perder cor por exposição solar e precisa de ter um revestimento com suficiente resistência à abrasão. Assim, o objetivo deste trabalho foi desenvolver e caracterizar um sistema de pintura à base de água para ser aplicado diretamente em folhas de cortiça. As principais propriedades estudadas foram o bloqueio à migração de taninos, a força de colagem a uma folha de PVC para aplicações em pavimentos e a aderência do revestimento à cortiça. O projeto foi dividido em cinco fases principais: 1) caracterização de solventes, 2) caracterização de resina, 3) seleção de aditivos anti-taninos, 4) seleção de cargas e 5) avaliação global dos resultados e ajuste da formulação, i.e., reformulação.

A caracterização do solvente foi realizada por meio de dois testes, avaliação da solubilidade dos taninos em diversos co-solventes e em água a diferentes valores de pH. Nove co-solventes foram selecionados e os melhores resultados foram obtidos com XXXX, XXXX e XXXX, que puderam ser utilizados na formulação subsequente e testados para ligantes, agentes anti-taninos e cargas Os taninos são menos solúveis se o pH for mantido entre 4-6.

A seleção da resina, aditivo anti-taninos e das cargas baseou-se nos resultados do teste de aderência ao PVC, adesão à cortiça e nos testes de migração de taninos. As resinas C1 e V1 mostraram ter propriedades apropriadas. O agente anti-taninos, XXXX, também apresentou características apropriadas para a resina R1. Além disso, o cargas F9 (XXXX) exibiu o melhor desempenho em manter o pH baixo do primário mas menor aderência. As mudanças na formulação usando C1 e R1 contribuíram para resolver o problema da aderência. Por outro lado, uma abordagem diferente, usando dois revestimentos, isto é, V1.1 como selante e O1.1 como um revestimento superior, foi introduzida na reformulação. V1 foi combinado com o F9 e o XXXX. O selante V1.1 foi aplicado para bloquear a migração dos taninos e o O1.1 foi usado para conferir opacidade e aderência ao PVC no acabamento.

A formulação composta pelo solvente XXXX, a resina V1 e O1, o agente anti-taninos XXXX e o cargas F9, foi a que permitiu atingir os objetivos propostos. A formulação desenvolvida tem grande interesse na proteção de cortiça.

Palavras chaves: Taninos, Cortiça, PVC, Tintas, Aditivo Anti-tanino.

Abstract

Cork is increasingly used as a flooring in homes, whether on pavements or on walls. When using cork in civil construction, it is common to protect it with paints and varnishes. But cork is a material that brings some problems: tannins that stain light-colored paints, tend to lose color through sun exposure and need to have a coating with sufficient abrasion resistance. Thus, the goal of this work was to develop and characterize a water-based paint system to be applied directly to cork sheets. The main studied properties were the tannin blocking performance, gluing strength to a PVC sheet and tackiness.

The project may be divided on five main phases: 1) solvent characterization, 2) resin characterization, 3) anti-tannins additives selection, 4) filler/extender selection and 5) overall assessment of the results and reformulation in order to successfully achieved the set goal.

The solvent characterization was performed using two tests, the solubility of tannin in a co-solvent and in water at different pH values. Nine co-solvents were selected and the best results were obtained with XXXX, XXXX and XXXX, which could be used in the subsequent formulation and tested for binders, anti-tannin agent and extenders. Tannins are less soluble if the pH is maintained between 4-6.

The selection of the resin, anti-tannin additive and fillers was based on the outcomes of the test of adhesion to PVC, test for tackiness, adhesion to cork and on the tannin tests. Resins C1 and V1 showed appropriate properties. The anti-tannin agent, i.e. XXXX, gave appropriate characteristics for the resin R1. Also, the filler F9 (XXXX) outcomes were the best in maintaining low pH of primer and less tackiness.

The changes in the formulation using C1 and R1 contributed to resolve the problem of tackiness. On other hand, a different technology, using two coatings, i.e. V1.1 as a sealer and O1.1 as a topcoat, was introduced in the reformulation. V1 was combined with filler F9 and XXXX. The sealer V1.1 was applied to block the tannin migration, and O1.1 was used to give opacity and adhesion to PVC in the topcoat.

The formulation composed by the solvent XXXX, the resin V1 and O1, the anti-tannin agent XXXX and the filler F9, was the best one to attain the proposed goals i.e. good adhesion to PVC, less tackiness, adhesion to cork, blocking action to tannins migration and good stability in climatic chamber tests. The developed formulation has high interest for cork sheets protection.

Key words: Tannins, Cork, PVC, Paints, Sealers, Anti-tannin additive.

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1 Introduction

1.1 Frame work

The work presented in this report was carried out under the course of Dissertation / Internship (DISEST) of the master's study program in the Chemical Engineering (energy sector and bio-refinery), in the School of Engineering of Porto. This stage took place in partnership with the Barbot - indústria de tintas S.A, welcoming company of the accomplishment of the internship in a business environment. The internship program was held at the Canelas Plant in the research and development department.

The stage lasted approximately 6 months elapsing between 1st March to 30th of August 2018.

1.2 Company presentation

The work took place within one of the largest companies Portuguese operating in the paint sector, Barbot - indústria de tintas S.A.
The Barbot company was founded in 1920 with the creation of a plant in Santo Ildefonso, in the district of Porto. All the graphics and the height of the packages were marked with the initials of the founder, Diogo Barbot. In 1958 built one more factory is situated in Laborim, belonging also to the Porto district under Carlos Aires Pereira, the father of the current administrator, Carlos Barbot [1].

Carlos Barbot took over the management of the company, after a tragic event that will forever mark the history of Barbot, which was the violent fire at the Santo Ildefonso factory, which completely destroyed the factory. In 2002, due to expansion policies and the need to respond to the market, a new plant was inaugurated in Canelas and since 2007 it has kept the two factories operating. [1] Barbot currently has an extensive distribution network, with 21 own sales outlets, not counting resellers. The company can be divided into the following companies, Barbot Portugal, Barbot Angola, Barbot Mozambique, Barbot Cape Verde and Jallut, still owning the brands Anpal and Sodulax (brands that have joined and created Masterpaint) [1].

This division of companies / brands only highlights the adventurous and constant search of taking their products further, operating in countries such as Spain, France, Belgium, Angola and Cape Verde, and has recently entered the Latin American market [1].

1.3 Theme and purpose of internship

The main objective of this report is to develop a water-based paint system to be applied directly to cork sheets. The main properties to be studied are the tannin blocking performance, gluing strength to a PVC sheet and tackiness.

1.4 Dissertation structure

The present work is divided in 5 chapters that go from the introduction of the theme, concepts inherent to the theme, experimental description, tests carried out with respective results and their discussion, and finally the conclusions and some suggestions for future work.

In the introduction, the framing project is presented. The host company for the development of the thesis was also the target of a brief description in this chapter.

In order to contextualize the study, the fundamentals that served as a basic for its development are described in the second chapter. This chapter deals with subjects such as the constitution of a paint, with a brief explanation of the function they have in the paint.

In the next chapter (third chapter), the developed activities and the obtained results are described. Initially, the study focused on different strategies to block tannins. Then, the next phase of results was to look for the final formulation that fitted the intended objectives by selecting each component, such as solvent, resin, anti-tannin additive and filler.

The conclusion, together with the future suggestions to be carried out, are outlined in the last chapter of this report. The conclusion, together with the future suggestions for work to be carried out, is the last chapter of this report, which sets out the appraisal of the methods and results achieved. The chapter closes with some proposals of procedures to be carried out in future work on the subject.

2 Concepts and fundamentals of work

2.1 Brief portriat of paint industry

Paint is a coating applied to the surface in form of a liquid dispersion, which then hardens forming a solid film. Looking around, we find paints and coatings virtually everywhere. We see paint on the walls of our homes or offices, and on furniture, refrigerators, washing machines, and toasters with nice colorful finishes. Outdoors, we see cars with an increasing variety of coatings. Building exteriors, equipment, bridges, pipelines, superstructures, and monuments are all painted with a variety of paints and coatings. There are virtually limitless products that use paint or coating on their surface [2].

Paints and coatings are applied due to many primary reasons, namely to provide aesthetic appeal, decorative value or specific attributes to the surfaces and products. Corrosion protection is the most important function of paints. Importantly, they should protect the part surface from the environmental factors (oxygen and other chemically active gases, moisture, dissolved salts and other chemicals, temperature, bacteria, fungi) [3].

Paints are classified as per functions of products and by their physical type. Classification of painting products by their functions [2]:

- Primers/undercoats
- Finish coat
- Sealers
- Varnishes

Classification based on their physical type are as follows [4][5][6][7]:

Solvent-borne paints contain up to 80% of solid constituents (binders, pigments and additives) dispersed in the organic solvent. Solvent-borne paints dry fast and may contain a wide range of binders. The main disadvantages of the solvent-borne paints are their toxicity and combustibility.

Water-borne paints contain water as the paint solvent. Waterborne paints are non-toxic and non-combustible, but they are characterized by long drying time due to slow evaporation rate of water. Reduced VOC emissions reduced fire and explosion hazardous waste. Water-borne paints based on water-soluble binders contain low molecular weight polymeric binders dispersed in water in form of true solutions. Water-soluble binders contain up to 15% of organic oxygen containing solvents soluble in water (alcohols, glycol ethers, etc.). True solutions can come the closest to resembling many conventional solvent-borne coatings. They can produce high-gloss, high-quality Water-borne paints based on polymer dispersions (Emulsion paints) contain 50-60% of high molecular weight polymeric binders dispersed in water in form of Colloids. Emulsion paint contain up to 5% of organic oxygen containing solvents soluble in water (alcohols, glycol ethers, etc.). Dispersions also dry by coalescence. They have a very high molecular weight that results in a paint film with excellent hardness and durability. These coatings can also air dry faster than other water types. One advantage of an emulsion-type coating is that it is possible to use high-molecular -weight polymers that will impart improved properties such as color retention, water and chemical resistance.

High-solids paints (Low VOC paints) contain more than 80% of solid constituents (binders, pigments) dispersed in an organic solvent. VOC - volatile organic compounds. High solids coatings contain the same basic ingredients as conventional solvent-based systems, but in different amounts. For example, the normal solids content for nitrocellulose resin coatings (typically used in the wood furniture industry) ranges from 8-30 percent. High solids coatings can achieve solids contents of 60-100 percent using acrylic and polymer binders. High solids coating formulations tend to use low molecular weight resins with highly reactive functional groups to aid in polymerization; coatings being used and tested include polyurethanes cured by isocyanate, polyesters, polypropylene, and acrylics. High solids paints can be applied to wood, plastics or metal, but the best results have been attained on metal substrates.

Powder coatings are obtained from powdered resin, particles of which are attracted by the electrostatic force to the substrate surface (electrodeposition). No solvent is involved in the process therefore powder coatings produce no/low toxic waste. The main disadvantage of powder coatings is high cost of equipment.

Radiation curable coatings are formed from a mixture of prepolymers, monomers and additives, which is cured under ultra-violet radiation. Radiation curable coatings harden fast and contain no solvents. The main disadvantage is relatively high cost.

2.2 Paints and their compositions

Paint is used to describe materials that have the major role of improving product aesthetics or decoration, such as interior wall paints. The term coating generally refers to materials that have a more protective role and provide long-term durability to products, which depends on the composition elements used in it [8].

Solidification process of a coating film, due to the evaporation of the solvents causing film-forming. Film forming ingredients, which are essentially polymeric materials, are called resins or binders. Resins and binders have the capability of forming transparent and adherent films. Pigments, which are finely divided insoluble particles, colored or white, have the capability of provided color and opacity when dispersed into a medium. In general, a paint or a coating consists of pigment dispersed in a resinous binder, reduced to an acceptable application viscosity with a *solvent*, sometimes water. The role of the solvent is essentially to provide a suitable consistency to the pigment/ resin mixture such that it can be applied uniformly as a thin layer. To control some properties of coatings such as viscosity, drying time, opacity, storage stability and ease of application, some specialty chemical compounds are added to the resin/pigment/volatile mixture, in small amounts, and are known as additives. A typical coating may have several such additives added to improve or modify specific properties. In general, all the ingredients of coatings are classified into the following four major raw material categories [8]:

- Resins or binders;
- Pigments and fillers;
- Additives;
- Solvents.

2.2.1 Resin

This term includes the total of the non-volatile components of a coating material (without pigments and fillers), which, during its processing, are responsible for the formation of the coating film. Their essential components are the film formers. As a rule, binders are synthetically produced, partly with natural raw materials modified polymers like alkyd resins, acrylates, isocyanates etc., which are employed in the form of solutions, dispersions or even of solid substances. Among all coating components, the binders influence most the range of properties of a coating material, because they are primarily responsible for the coating material's weather resistance, chemical stability as well as mechanical resistance. Binder is the main ingredient of paints. Binders are polymers (resins) forming a continuous film on the substrate surface. Binders are responsible for good adhesion of the coating to the substrate. The binder holds the pigment particles distributed throughout the coating. The binder is dispersed in a carrier (water or organic solvent either in molecular form (true solutions) or as colloidal dispersions (emulsions or sols). Resin are differentiated based on the chemistry type, ionic character, solids content and ph. Common binders used with different chemistry are Alkyd resins, Acrylic resins, Phenolic resins, Urethane resins (polyurethanes), Epoxy resins, Vinyl's, Polyesters, Styrene-butadiene etc. [2][6][8].

Benefits of using resin to give following properties to a finished product paint [8, 9]:

- Chemical stability;
- Excellent toughness, hardness and flexibility;
- Continuous, adherent and uniform film;
- Thermo-mechanical and optical properties;
- Broad range of compatibility;
- Good shelf-life under normal storage conditions;
- Durability – resistance to abrasion, water, chemicals, UV rays, heat, etc.
- Gloss;
- Fast-drying coating;
- Stain resistance;
- Excellent weathering properties, moisture and corrosion resistance;
- Provide excellent adhesion;
- Low toxicity and flammability due to low VOC levels;
- Help reducing air emissions;
- Advantage in reducing cost in some cases, with no usage of additives, thinners, or hardeners.

Ionic character of resins

An anionic emulsion has a negative charge, a cationic emulsion has a positive charge, and a non-ionic emulsion has no charge. Amphoteric emulsion has positive as well as negative charge as shown in the figure 2.1. The emulsion act as a substrate so to attract the opposite charge possess by any constitution of coating for example additive, fillers etc. for good adhesion. Therefore, when applying a cationic emulsion to an anionic substrate there is usually better adhesion. Cationic emulsion tends to have better adhesion properties than an anionic emulsion because of the positive charge. Most of the research and development, formulating, and lab testing have been done in the industrial coatings industry to make coatings from anionic systems [10, 11].

A cationic emulsion presents more of a challenge to get it to work with additives. The reason is because some of those chemicals added may be anionic. This will result in the emulsion turning into a solid. So most of the time there are chemicals that are non ionic that possess no charge that are used as additives to formulate and manufacture coatings [10,11].

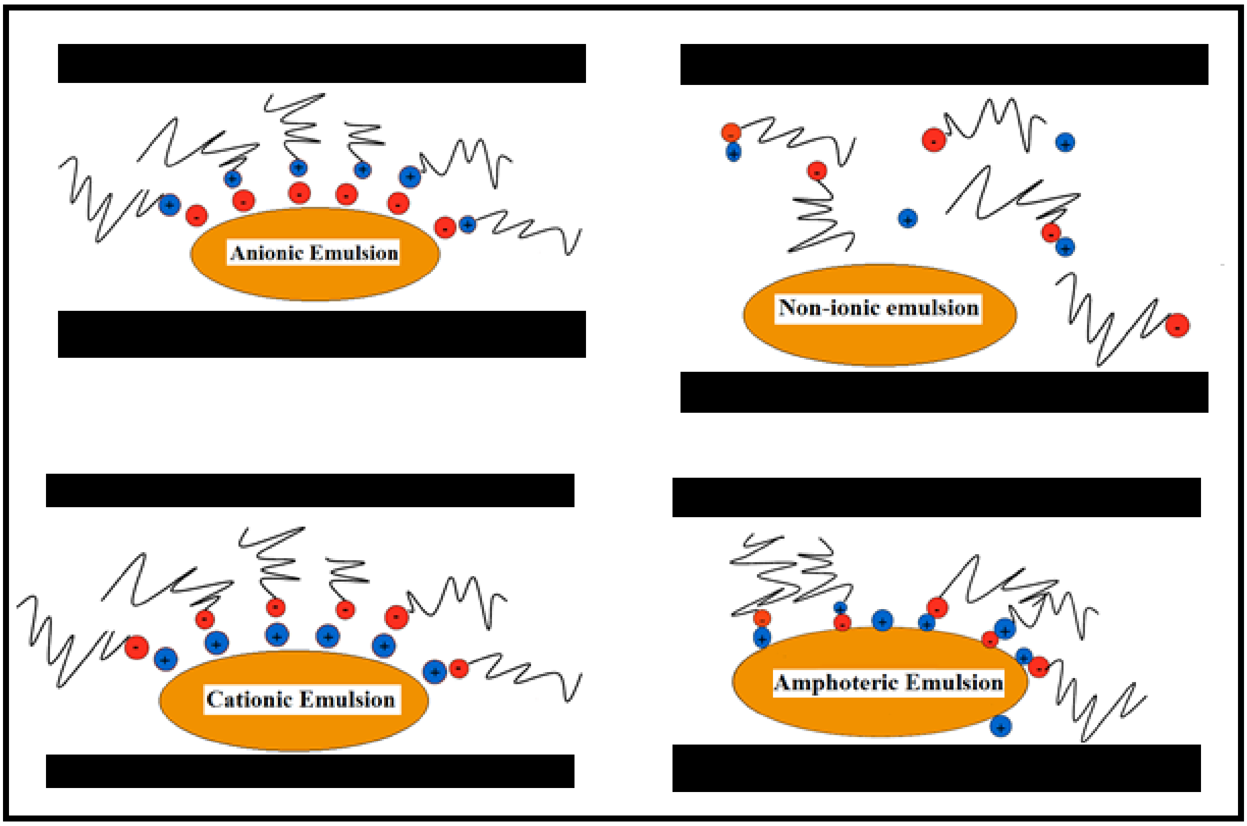

Figure 2.1- Ionic character of resins[12]

2.2.2 Pigments and fillers

Properties such as color, opacity and high refractive index that the binder alone cannot provide, pigments and fillers fulfill this property. Fillers and extenders are also referred to pigments. Pigments and fillers can also overlap, depending on the application. One of the more important reasons to use fillers in paints is to lower the cost of the product. Filler is a substance consisting of particles which is practically insoluble in the application medium and is used to increase volume or to improve technical properties, to increase the paint film thickness, to impart toughness or abrasion resistance and to influence optical properties to the coating [6][13]. Examples of fillers and extenders: Carbonates, Dolomite, Silicates, Talcum, Kaolin, Mica, Feldspar, Quartz sand (SiO_2)**,** Baryte ($BaSO_4$)**,** Kaolin Clay**,** Limestone etc**.** [6]

Pigment is a substance consisting of particles which is practically insoluble in the application medium and is used as a colorant or various property for example as inorganic or organic pigments, colored pigments, white pigments, effect pigments, anti-corrosion pigments, magnetic pigments, depending on their chemical composition, optical or other technical properties. If the substance helps to increase opacity, then it has the characteristics of a pigment. If it behaves transparently, though, it is a filler. In general, materials with a high refractive index (≥ 1.7) are pigments. All other mineral materials with a similar refractive index, like organic polymers, belong in the category of fillers [6] [13].

Pigments may be natural, synthetic, inorganic or organic some commonly used in paints**:** Titanium Dioxide**,** Zinc Oxide**,** Yellow Dyes**,** Chrome Oxide Green**,** Phthalocyanine Blues**,** Pigment Brown**,** Carbon Black**,** Iron Oxide etc. [6].

Benefits of using pigments and fillers to give following properties to a finished product paint: [13]:

- Impart it a color, opacity (hide the substrate surface).
- Protect the substrate from UV light.
- Change appearance such as color, opacity and mechanical properties.
- Increase hardness and decrease ductility.
- Act as Corrosion inhibition.
- Gloss and Sheen.
- Depending upon particle size, shape and amounts used, the barrier properties of pigment coatings vary. barrier properties of coatings.
- Absorbing UV light and thus protecting the film from degradation.
- Rheological properties, which play a vital role in storage and application of coatings
- Antifouling properties, infrared light absorption or reflection.
- Ease of Dispersion.
- Spreading rate.
- Optical properties such as Whiteness, Brightness, Yellowness index and Refractive index.

2.2.3 Solvents

Solvent (water or organic solvent) is a medium where the binder, pigment and additives are dispersed in molecular form (true solutions) or as colloidal dispersions (emulsions or sols). Solvents (thinners) are also used for modification of the paint viscosity required for the application methods: brush, roller, dip, spray. The solid coating is formed due to evaporation of solvent therefore the evaporation rate is one of the important properties of solvents. Other important properties are the ability to dissolve the paint ingredients and toxicity [6] [14].

To facilitate film-forming an organic solvent, such as butyl glycol, Texanol, Dipropylene glycol, Butyl glycol acetate, etc. are added. They are called as coalescence agents also "film-forming additives which show a good water miscibility and are added to aqueous film former dispersions in little amounts [8].

Solvents help in the wetting of pigments and coating substrates and the regulation of important properties, during the film formation, like compatibility of the coating components, levelling and gloss. If solvents are only added to the ready coating to regulate its working viscosity, they are normally called "thinners". Organic solvents are the main cause of fire and explosion danger in the coating industry and therefore they generate high costs in prevention measures. For several years coating research and development have had as a main target the elimination or reduction of the solvent amount in coatings (" low-solvent and solvent-free) [8].

2.2.4 Additives

. **Additives** are small amounts of substances modifying the paint properties, some *e*xamples are [6, 9]:

- **Driers** accelerate the paints drying (hardening) by catalyzing the oxidation of the binder.
- **Coalescing agents** (or co-solvents) used as a filmification agents that help the resin to filmificate properly.
- **Plasticizers** increase the paints flexibility.
- **Fungicides, Biocides and Insecticides** prevent growth and attack of fungi, bacteria and insects.
- **Defoamers** prevent formation of air bubbles entrapped in the coatings.
- **UV stabilizers** provide stability of the paints under ultra-violet light.
- **Anti-skinning agents** prevent formation of a skin in the can.
- **Adhesion promoters** improve the adhesion of the coating to the substrate.
- **Corrosion inhibitors** reduce the corrosion rate of the substrate.
- **Wetting and dispersing agents** that aid the incorporation of pigments and extenders in the paint.
- **Thickeners** act as a proper rheology modifier to provide a good balance of properties like storage viscosity, anti-settling properties.

- **Flow and leveling agents** are to enhance a film's flow and leveling to eliminate surface defects such as brush marks, orange peel and craters.
- **Matting agents** allow better control in low-gloss finishes for reasons such as roughness, tackiness into the surface of the coating film.
- **Stain-blocking additive allows to control stain migration on the top coat.**

2.3 Paint production

2.3.1 Preassembly and premix

The first step in the manufacturing process is preassembly and premix (Figure 2.2). In this step, the liquid raw materials (e.g., resins, solvents, oils, alcohols, and/or water) are "assembled" and mixed in containers to form a viscous material to which pigments are added. The pigment and liquid mixture form a thicker material, which is then sent to the grinding operations [15][16] [17] [18].

2.3.2 Pigment grinding/milling

The incorporation of the pigment into the paint vehicle to yield a fine particle dispersion is referred to as pigment grinding or milling. This Dispersion process occurs in three stages which may overlap in any grinding operation. The wetting process begins in the premix step, when the pigment is charged to the liquid vehicle. Below are the three stages pigment grinding:

- Wetting of the pigment particles by the fluid components of the mill base.
- Breakdown of the associated particles (agglomerates and aggregates) leading to smaller particle sizes.
- Stabilization of the dispersion preventing renewed association (flocculation).

This process is mechanical breakup and separation of the pigment particle clusters into isolated primary particles. Pigment particles based on three classes Primary particles (crystal), Aggregates (Primary particles with surface to surface contact) and Agglomerates (Primary particles touching each other via edges and corners).

The goal of pigment grinding is to achieve fine, uniformly-ground, smooth, round pigment particles which are permanently separated from other pigment particles. The equipment used dispersion for this practical "High-speed disk dispersers". It includes

Essentially, the high-speed disk disperser consists of a circular, steel, saw-blade-type impeller attached to the end of a steel shaft as shown in figure 2.3. The disk is suspended in a mixing pot which may be jacketed for water-cooling. With the principal of actual dispersing system consists of a chamber and a rotor; the chamber is filled with grinding media and the product to be dispersed. The actual particle size reduction is accomplished by the moving grinding material, which is activated by a high speed and high energy agitator. The speed is increased once initial wetting is done in preassembly and premix stage as it requires slow speed after which the speed is increased while reaching to the grinding stage. Variable speed systems can handle all stages in the preparation of paints (i.e., preassembly and premix, pigment grinding and dispersion, and product finishing) in one piece of equipment.

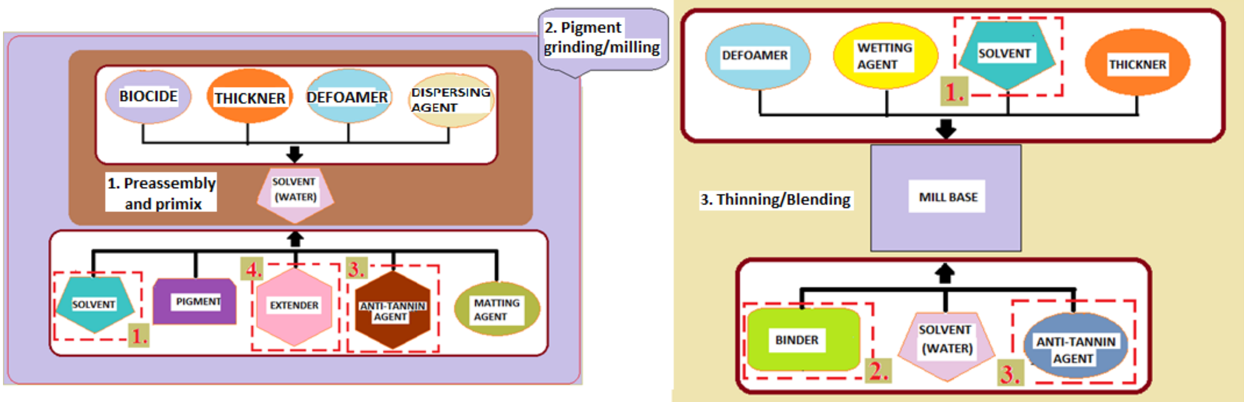

Figure 2.2 - Three steps for paint production i.e. Preassembly and premix, Pigment grinding/milling and Product finishing/blending.

After liquid raw materials (e.g., resins, solvents, oils, alcohols, and/or water) mixed in premix stage, under moderate speed pigments and fillers are added slowly. The impeller speed can be increased until the doughnut effect is detected at a higher rpm. After this premixing step the dispersion is carried out at high peripheral speeds that correlate to the tip speeds used in production by maintaining the doughnut. Dispersing small quantities will require high rotational speeds to match production results.

As the grinding material collides and rolls about each other, the solid particles get caught between them and are gradually reduced in size. Each primary particle or aggregate in the finished product is the result of billions of bombardments by the grinding media. The quality of the dispersion degree is dependent on the mechanical power input which is influenced by the torque transmitted by the shaft onto the mill base. Below figure 2.3 shows the laminar flow pattern which is obtained when the diameter of the vessel and the impeller as well as the distance between plane of disc and base of the vessel are matched to another.

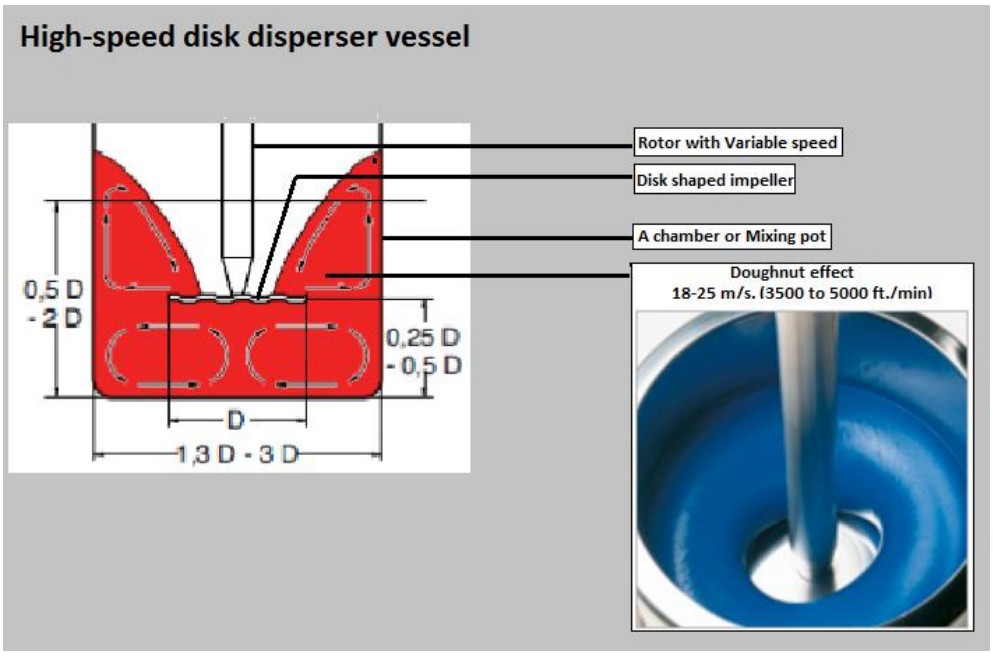

Figure 2.3 - High-speed disk disperser vessel [24].

After grinding is done which can be completed by measuring the Fineness of Grind by grind guage also called as Degree of pigment dispersion. The range depends of type of coating. Topcoats for the automotive industry typically are grinded to 5 microns. Decorative wall paints can go up to 50 microns.

2.3.3 Product finishing /blending

Product finish involves thinning and blending. In thinning process material is letdown after complete mill base dispersion with solvent and/or binder to give a coating which is designed to provide a durable, serviceable film that is easily applied to the substrate. The volume of the paint may increase significantly at this point depending on the final product specifications. Blending operations occur once the necessary additions have been made to the completed mill base dispersion. Blending is the process of incorporating the additions into the material in order to meet the desired product specifications.

2.4 Cork as a construction material

Cork is a material with applications that have been known since ancient times, it was mostly seen as a floating artifact and a closure, some of them related to building. A material that comes from the cork oak, which is an astonishing tree, very long-lived and with an enormous capacity for regeneration. It can live on average 150 to 200 years, despite its bark being stripped around 16 times during its lifetime, at nine-year intervals. Cork is a *parenchyma suberose* originating from the meristem suber phelloderm of the cork oak (*Quercus suber L*.), consisting of the covering on the bark and branches of the cork tree [19].

The main target sector of cork products is the wine industry which accounts for 70,1 percent of what is produced, followed by the construction sector with 26,3% - including floors, insulation and coverings, blocks, plates, sheets, strips and other cork products such as home and office decoration, raw material (3.6%). Cork oak forests are of crucial importance to the economy and ecology of several Mediterranean countries, covering a worldwide area of 2,139,942 hectares. Portugal has 34% of the world's area, which corresponds to an area of 736 thousand hectares and 23 % of national forest. The cork oak is the second most dominant forest species in Portugal. World cork production rose to 201,000 tonnes, highlighting Portugal once again as the leader in production, with 49.6% and 100,000 tonnes, which are classified 30% Thin cork, 25% Scrap By-products / Waste, 5% Bits pieces and 40% Rolls cork stoppers. Cork stoppers continue to lead Portuguese cork exports, accounting for 70.1% of the total (corresponding to 592.6 million euros), followed by cork as a building material with 26.3% and 222,6 million euros [20].

The most common cork products used in building are: thermal, acoustic and vibration insulators (walls, ceilings, flooring); suspended ceilings; wall coverings, flooring and ceilings; baseboards; linoleums; granules as fillers and mortar mixtures; insulating, expansion or compression joints; and for industrial purposes: anti-vibration for machinery and insulation for industrial cold storage. Agglomerated cork for thermal insulation for buildings (ceiling, flooring and walls) namely, for the protection of concrete from attaining thermal amplitudes, for reducing energy losses, protecting flooring surfaces and, in addition, hindering, obstructing or reducing superficial water condensation on walls and ceilings. In the acoustics field, it is called acoustic correction by acoustic absorption and reduction in the reverberation time of certain environments, in addition to diminishing or reducing impact sound transmission in special applications [19, 20].

Due to cork's high compressibility and recovery, certain types of composition cork are used as expansion joints between rigid elements, such as concrete slabs. Placed between the flooring/paving and the subfloor of the construction, they also help provide good sound and even thermal insulation. Below figure 2.4 showes applications of cork in various fields [19, 20].

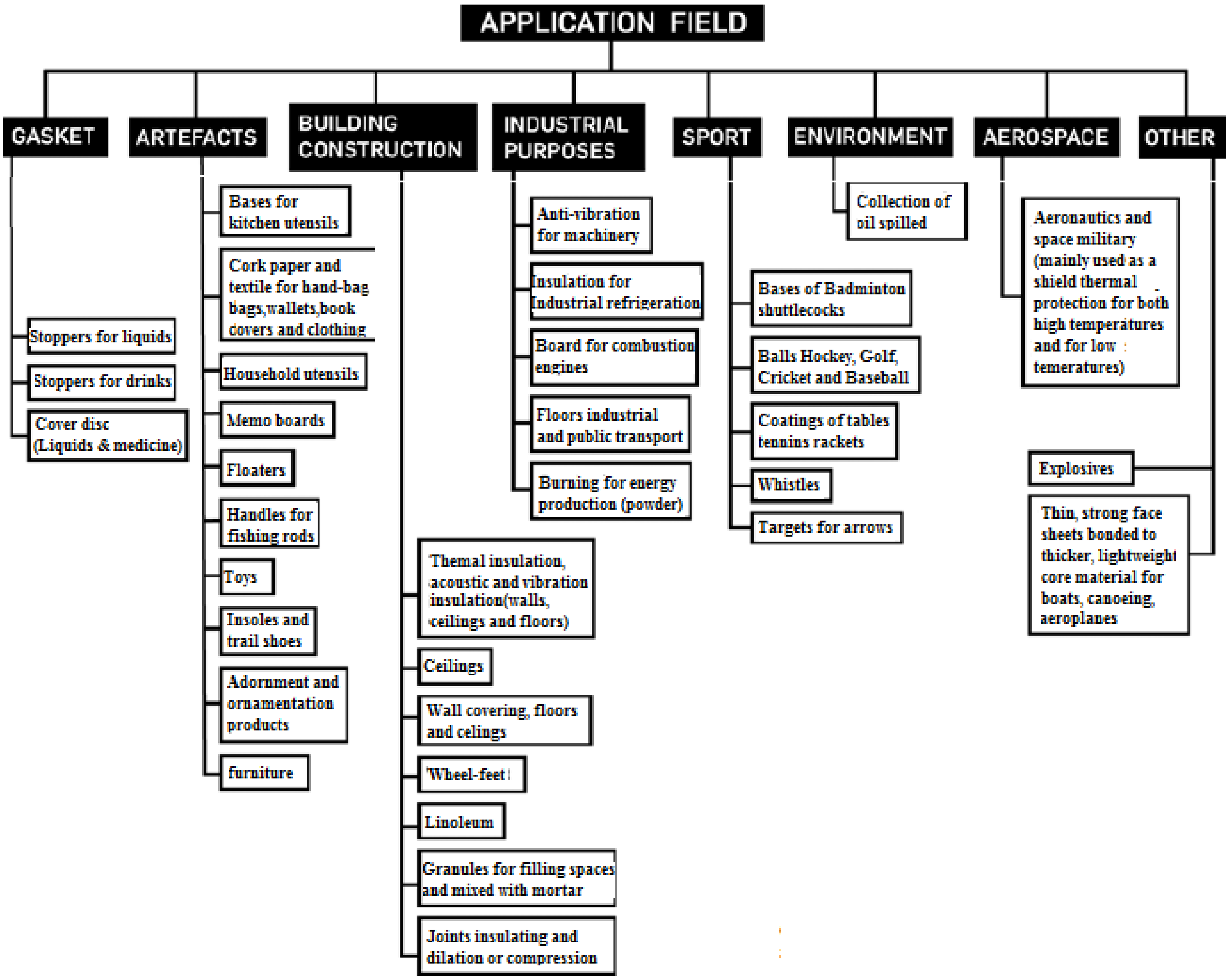

Figure 2.4 - Application of cork in various fields [21].

2.5 Cork sheets

Macroscopically, cork is a light, elastic material, low thermal conductivity, practically impermeable to liquids and gases, a thermal and electrical insulating material and acoustic and vibration absorber, being also innocuous and practically incorruptible, providing a compression capacity with practically no lateral expansion. Microscopically, cork is composed of cell layers, alveolar in shape, whose cellular membranes have a certain degree of impermeability and are full of a gas, usually considered like air, occupying nearly 90% of its volume [19, 22].

The first harvesting (known as *"desbóia"* in Portuguese*)*, produces cork called virgin, with a very irregular exterior surface. Successive harvestings give birth to cork with a more uniform exterior surface, known as reproductive cork or amadia. The first reproductive cork, still with some irregularities, has the specific name of "*secundeira*" (in

Portuguese), and like virgin cork is mainly used for grinding, to obtain granules, for the subsequent production of agglomerated cork. When pruning the cork tree branches, a byproduct – "*falca"* - is obtained, a mixture of virgin cork, inner bark and wood, traditionally removed with an axe [19].

Granulates are made by grinding scraps, parings, virgin cork, cork pieces or stopper production waste and are mainly used as raw material for the manufacture of agglomerates. Granulates are obtained from different kinds of milling actions, depending on the material to be ground and the type of granules desired. The granulation process is like what is carried out on other types of agglomerated cork. The granulometry that is finally obtained is dependent on the job function of the agglomerate [19, 21].

Expanded Agglomerate is made through a process agglutinating granules of crude virgin cork, mainly *falca* (which has a high extractive level and functions as a natural inter-granular binder) and other types of cork of inferior quality. The agglomeration is carried out by the autoclave process which also works as a mold. The granules are subjected to heat and pressure, with superheated steam. These are usually produced in the form of boards of different thicknesses, followed by corrections in size and squareness. This is a natural product, of vegetable origin. No synthetic agents are used; therefore it is a product with excellent ecological characteristics. These agglomerates were considered a strategic material used in multiple applications as like mentioned in figure 2.5. The process shown in the figure 2.6 gives the overview production cork sheets [19, 21].

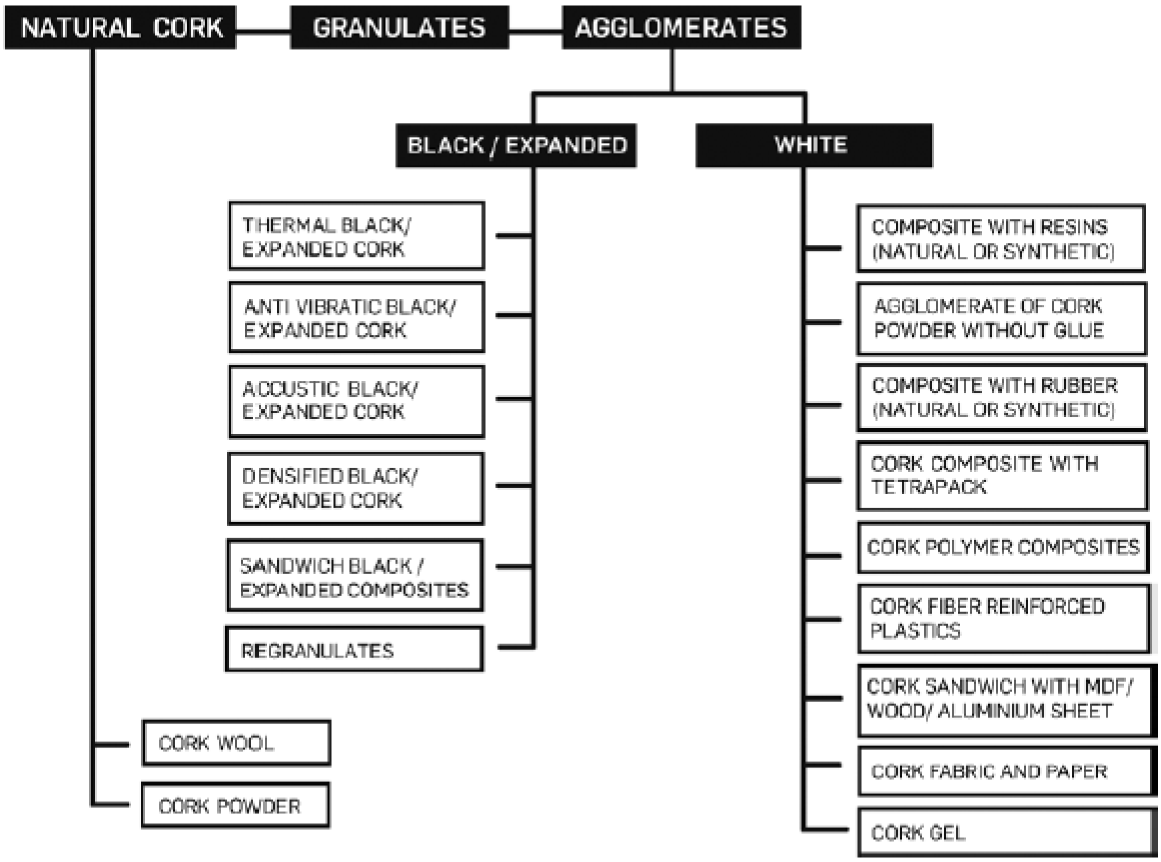

Figure 2.5 - Schematic Portfolio of Cork Materials [21].

The composite agglomerate best known and most widely used in industry is white agglomerate. It is a mixture (granules + agglutinant + optional agents), made from waste products from the transforming cork sub sector and represents a means of giving value to waste and an excellent opportunity to recycle (used cork stoppers) or re-use cork products. By maintaining all the properties of cork and being able to acquire extra characteristics, it can take on numerous forms and combinations and therefore occupies an advantageous position compared with other composite materials. Agglomerates are made from a process of agglutinating the cork granules with a specific, pre-determined granulometry and density, through the joint action of compression, temperature and an agglutinating agent, depending on the final product desired. The most common process uses synthetic resins of polyurethane, phenols and melamine, and sometimes also resins of vegetable origin, to give a mixture of granulate and resin. In most industry uses, the agglomerates are usually produced in molds, which are normally metal for the manufacture of blocks or rolls, which it is then possible to laminate [19, 21].

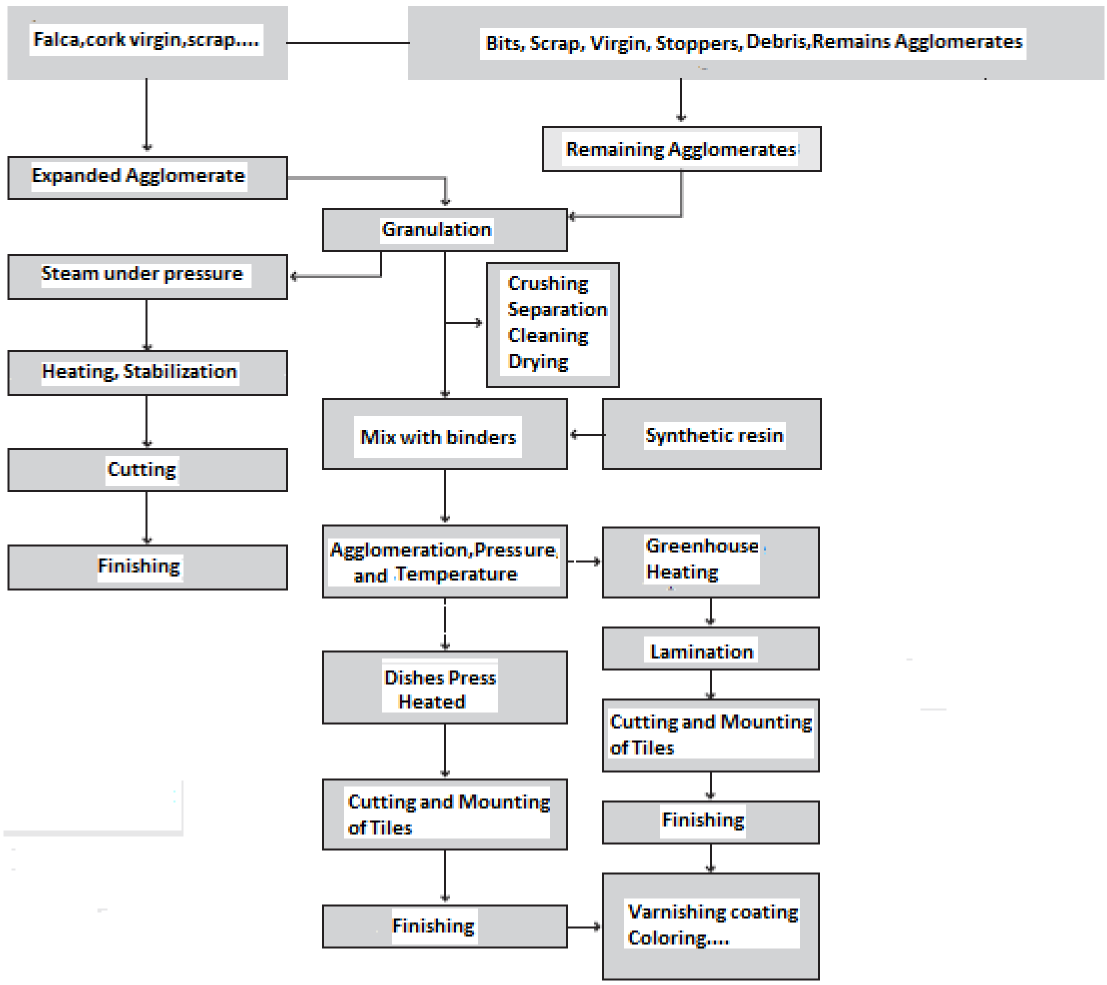

Figure 2.6 - Integrated scheme to produce cork products for construction [23].

The sheets thus formed, can undergo various types of surface treatments: wax, varnish, various film coverings (for example, PVC) or even paint. In figure 2.7 shown various surface treatment of cork sheet starts with cork sheet with PVC coating from left moving towards right sheet coated with a combinations of different color primer. When varnishing, a synthetic varnish (acrylic or polyurethane) is usually applied, followed by a treatment of Ultra Violet Radiation (UV) or by means of a forced hot air tunnel dryer [19, 21].

White agglomerates can be used in molding, turning or cutting processes for many different purposes, from civil construction (coverings, insulation) to industry (automotive, aeronautical) or home products (furniture, accessories). The various types of decorative items and coverings are obtained by means of a simple cork sheet or by overlapping several types of agglomerated cork or laminated natural cork, or yet, by the composition of cork with other materials, namely agglomerated fiber or wood particles. This gluing operation is usually carried out with the aid of rollers or a press. Examples of white agglomerates shown in figure 2.8 which is used in project for the objective. Figure 2.7 shows the example of cork sheet surface treatment with PVC coating which involves, first coating with anti-tannin primer followed with PVC sheet. Visualize the color of the surface precisely which is yellowish and not white. The yellowness of the primer is due to tannin migration present in the cork, to overcome the yellowness to a pure white color which means tannin free primer is the objective of the project [19, 21].

Figure 2.7 - Examples for surface treatment of cork sheet. From left to right PVC coating, different color primer coating.

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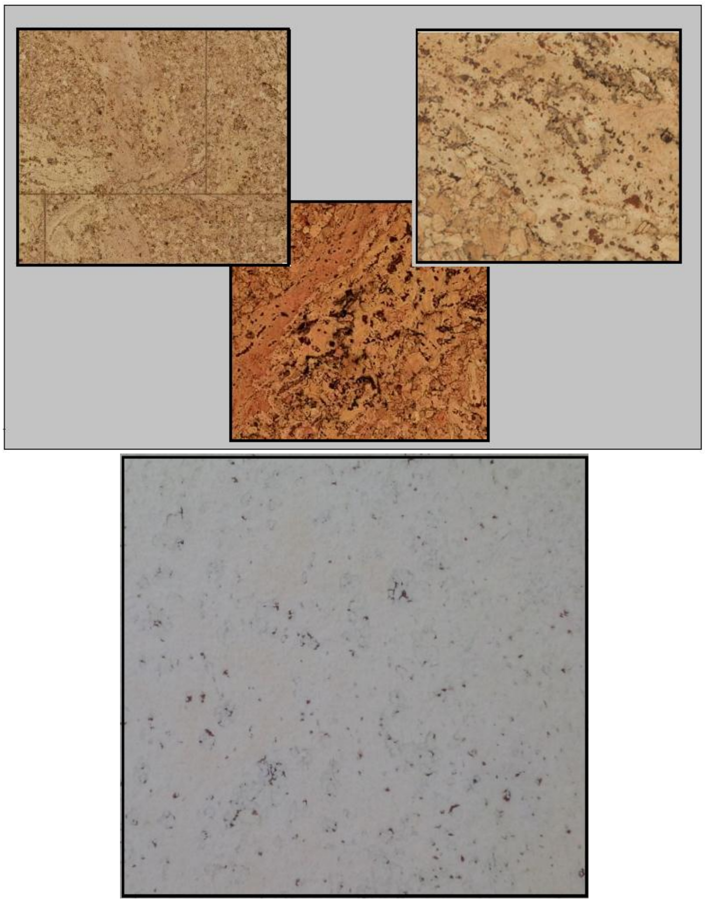

Figure 2.8 - Examples of white agglomerates and example of cork sheet surface treatment with PVC coating.

2.6 Tannin chemistry

Tannins were researched extensively due to the persistent problem that they present when painting certain wood. Tannins are naturally occurring, plant-based polyphenolic compounds found in cork, including wood used in constructing homes and commercial buildings. They provide color and protection/preservation to the cork. Over time, it is possible for tannins to migrate, or bleed, from the cork into coatings, causing significant yellow to brown discoloration in the case of tannin-rich cork. The main component of tannins is penta-metadigalloyl-glucoside, a derivative of gallic acid (3,4,5 – trihydroxybenzoic acid). The typical tannin structures are represented in Figure 2.9 [24].

Tannins form a water-soluble compound when exposed to the basic conditions typically associated with paints. It is generally believed that using a water-based primer preventing migration of tannins into the topcoat. However, there are ways of preventing migration and staining using a waterborne primer, including: 1) the use of active pigments or blocking agents, such as compounds of zinc, aluminum, or titanium, 2) the introduction of definite functionalities, such as urethane or alkyd-urea groups, and 3) the use of amphoteric block copolymers. For example, waterborne primers will most likely be more effective at preventing tannin bleed if they are formulated for fast drying, with a maximum amount of solids and a minimum amount of co-solvents. Primers with a near-neutral pH will also have a better chance of preventing tannin bleed, due to the need for a basic environment for the tannins to form water soluble compounds. Other properties of primers, including the flexibility, sand ability, scrub resistance, and adhesion, are important for successful tannin blocking [24].

The chemical composition of cork includes several types of compounds, which are traditionally divided into five groups [19]:

a) Suberin (45% - responsible for cork’s compressibility and elasticity);

b) Lignin (27% - structure of the cell walls);

c) Polysaccharides (12% - also linked with the structure of cork);

d) Wax (6% - repels water and contributes to its impermeability);

e) Tannins (6% - color and protection/preservation of the material) and

f) Ash (4%)

A staining problem develops during the drying and film forming stage when tannins migrate outward, due to the water present in the painted cork. The driving force for this is the interfacial humidity exchange, where water acts as an eluent. It is still not known for sure if the migration of tannins stops when hydric equilibrium is reached [24].

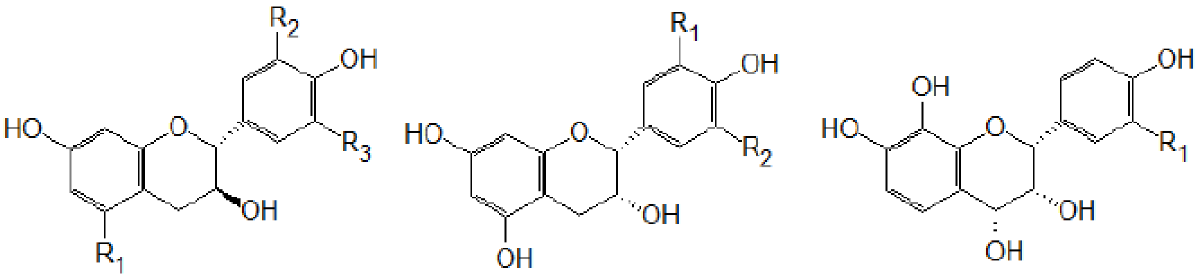

Figure 2.9- Typical tannin structures [24].

3 Materials and Methods

3.1 Viscosity

The most frequently employed devices to determine the viscosity is the flow cup (figure 3.1). The test is described in ISO 2431:2011 “Determination of flow time by use of flow cup”. It is a viscometer that shows the flow properties of liquid substances. The application of the cork sheets is done by an industrial roller. The viscosity in the flow cup in this type of application is typically low i.e. below Below 35s in a flow cup ISO 4. The viscometers, which are usually employed for coatings, can be subdivided into two groups, according to their measuring principle: those where the shear (" *viscosity*) is caused by the effect of the force of gravity and those where it is produced by a mechanical rotation. The " *flow cup*” belongs to the first group [25].

Figure 3.1- Flow cup.

3.2 Rheology test

The main objective of this test was to see if the rheology profile of the paint was Newtonian. This type of profile is when viscosity (flow properties) only depends on the temperature. The rheology tests were done using the rheometer Anton Paar MCR102 (figure 3.2) that already has some predefined programs. However, the trials are customizable both at the test parameter level and at the level of more actions. The flow curve test were performed, using the cone-dish measuring system. In the "flow curve" test, the test was customized to remove 45 points with cut-off rates between 0,001 and $1*10^4$ s^{-1} with logarithmic variation. [26, 27].

Figure 3.2- Anton Paar MCR102 Rheometer.

3.3 pH-value

pH is important because tannin solubility depends of the pH. The equipment used was a pH meter HI 2020 (pH) by hanna instrument [28].

3.4 Degree of pigment dispersion

Solid particles such as pigments and fillers are important components of paints and need to be dispersed and stabilized well in the formulations to assure consistent color, quality and durability. Simple device to evaluate the degree of dispersion of pigments and fillers (extenders) in mill bases or in coating materials is called grind meter and can be as grind gage or Hegman gage. Many types of solid materials must be ground or milled into finer particles for dispersion in appropriate liquid vehicles. The procedure is based on ISO 1524: 2000 "Determination of finess of grind ". The tests were made with a grind meter 100µm having a scale in Micron 0 - 100 and Hegman 8 - 0 performing an error +/- 2 µm was applied. All tested formulations were able to meet the goal of 20 µm or 7 hegman with identical times of grinding, of around 15 minutes [29, 30].

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3.5 Settling test

The settling test is based on the stability of the paint after storage. It is performed when the sample primer is prepared, that sample is kept for a period. An observation is made which is a formation of certain pigmented paint, during storage, a compact sediment. The sediment consists of pigment or filler (extender) particles, enwrapped by film former which, due to their density, during time sink to the ground. The sample has been kept for two months under observation, which is once in every week [14].

3.6 Spectrophotometer

Opacity is measured directly by using a spectrophotometer (Figure 3.3). The paint sample is drawdown using a wire-wound rods called as applicator. The applicator used gives thickness of 100 μm wet liquid film. Wire-wound rod is recommended to give very thin film uniform drawdown on a Contrast Chart. Charts comprised of a simple combination of black and white areas with ample space for reflectance measurement. Opacity drawdown charts are used to test the hiding power of coatings using Spectrophotometer. The spectrophotometer used is Data color Spectrum 400 TM with the program CIELAB. For verifying this test is based on ISO 6504-3:2006 “Determination of contrast ratio of light-colored paints at a fixed spreading rate” and ISO 7724-2:1984 “Color measurement” [31] [32].

Spectrophotometer is also used to see color difference of test panel kept for 1000 hours in QSUN and QUV chambers. Color difference can be measured using numerical equation 3.1 referred to Delta (ΔE*) and measuring values of CIE L* a* b* coordinates from Data color Spectrum 400 TM. L* a* b* color space was modeled after a color-opponent theory stating that two colors cannot be red and green at the same time or yellow and blue at the same time. As shown in figure 3.3, L* indicates lightness, a* is the red/green coordinate, and b* is the yellow/blue coordinate. Deltas for L* (ΔL*), a* (Δa*) and b* (Δb*) may be positive (+) or negative (-). The total difference, Delta E (ΔE*), however, is always positive. The colorimetric values (CIE L* a* b**) of test panel before the test and after the test are measured and ΔL* or Δa* or Δb* i.e. (L* After reading minus L* Before reading) is calculated. Further putting the values of ΔL, Δa* and Δb* in equation 3.1 ΔE can be calculated. ΔE is used identify inconsistencies and help to control color more effectively [33][34].

$$\Delta E* = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2} \quad \text{Equation 3.1}$$

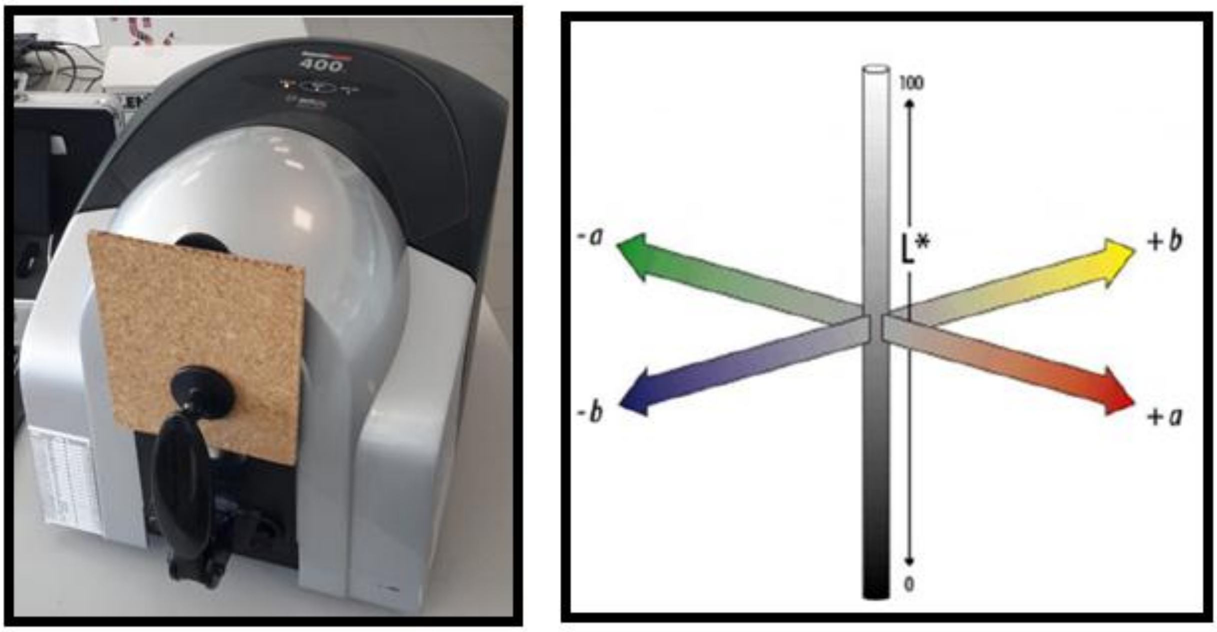

Figure 3.3- Spectrum spectrophotometer Data color 400™ and CIELAB coordinates [35].

3.7 Gloss

The method used for the measurement of brightness is governed by Portuguese Standard 3631 which is based on ISO 2813. With BYK micro-Tri-gloss, (Figure 3.4), the measurement is made from 3 different angles simultaneously: 20º,60º and 85º degrees. According to the gloss degree ranges, different measuring geometries must be applied. Using the standard value shown in the table 3.1 for differentiating the gloss range of the samples [36].

Table 3.1- Standard gloss range(Gloss units).

Gloss Range	60° value	Measure with
High Gloss	> 70GU	20°
Semi Gloss	10 - 70GU	60°
Low/ Matt	< 10GU	85°

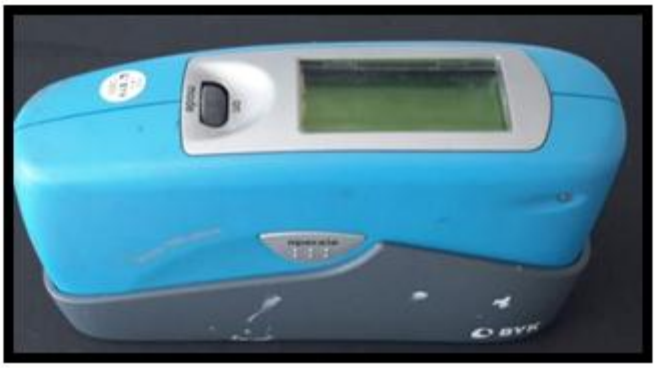

Figure 3.4- BYK micro-Tri-gloss **used for reading the brightness.**

3.8 Tannin test

The goal is to have a system that blocks tannins it is seen visually by draw down of primer sample in a cork sheet using wire-wound rods applicator which gives a wet thickness of 100 µm. After applying let it be for drying if tannins are already migrating on the surface of the primer it can be easily before drying by observing yellow spots on the surface. After drying completely under room temperature i.e. 25°C, it comes under 3 observations. First as mention before if migration of tannin on the surface before drying as on wet surface and after drying it can be seen many yellow spots, which results in “Fail” that mean the sample as no property of blocking tannins and it can be improved by addition or anti-tannin additive or other filler or doesn’t have the ability. Second, the appearance of tannins on surface is less as comparing to first which gives the result of “INCONCLUSIVE”, the blocking can be improved as it has less affinity to tannins and can easily be improved by adding anti-tannin additive or other fillers. The third and final one is what the project is about of complete surface without tannins as tannin free results shown is “Pass”, which shows no affinity with tannins and not required any additive of fillers for further improvement. Figure 3.5 shows the results in which red circles with stains spots are on the surface of the primer.

Figure 3.5- Visual observation made for tannin test.

3.9 Adhesion to cork

The objective of this test is to verify the paint adhesion of films by the method of the grid, which consists of making two cuts perpendicular to each other with a Multiple blade, forming a square on the film with about 2 cm of length. The next step is to place over this area, tape duct, boot and verify that entrains the squares of the substrate. Instrument used is shown in figure 3.6. The results are estimated according to ISO 2409: 2013 "cross cut test" [37].

Figure 3.6- Cutting instrument used to perform the test of adhesion.

3.10 Adhesion to PVC

The objective is to have a system that blocks tannins and glue to the PVC sheet. The test assesses the adhesion of the primer to PVC sheet which is done after tannin test, which is also by visual observation. Cork panel and PVC sheet are cut in equal sizes and submitted to a pressure (8 bar) at 140ºC for 1 min where PVC is placed on applied primer part of cork panel. After cooling down, it is meant to remove the PVC sheet gently. Results based on three observations are shown in figure 3.7. 'Fail' if the pvc sheet is removed easily along with primer. 'Pass' if it is hard to pull out PVC sheet without primer on it, results in best adhesion towards PVC.

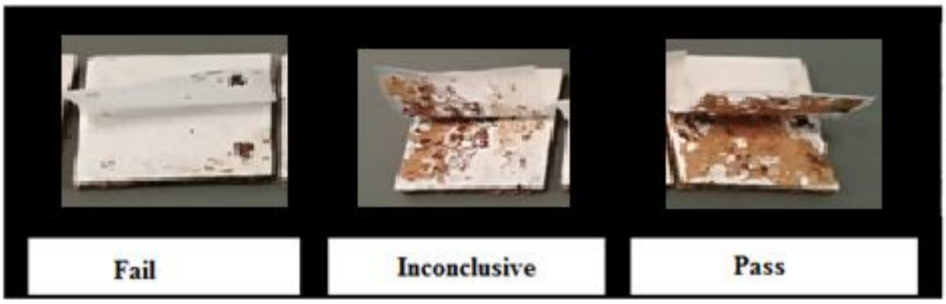

Figure 3.7- Visual observation made for Adhesion to PVC.

3.11 QUV- accelerated UV exposure

The accelerated aging test was performed according to ISO 11507 "Exposure of coatings to artificial atmospheric conditions - Exposure to UV and water fluorescent lamps". In this standard there are two methods, one that has condensation and another that has water spray. What was applied was method A, which is that of condensation. The program is cyclic, there is 4 hours of irradiation and 4 hours of condensation. It is necessary to pay attention to the phase of the cycle in which the program is under examination of the coatings. This can interfere with the properties of the paint (water absorption in the condensation cycle may have influence). The assay lasted 1000 hours and the lamp used was UVA-340. Using Spectrophotometer color difference of test panel is calculated. The apparatus used for the tests is LU-0801 model from Q-lab is shown in Figure 3.8 [38, 39].

Figure 3.8- Q-Panel Lab Products QUV.

3.12 QSUN- accelerated sun exposure

The accelerated aging test was performed according to ISO 11341 standard "Artificial weathering and exposure to artificial radiation- Exposure to filtered xenon-arc radiation". In this standard there are four cycles, two based on wetting the test panel i.e. A, B and other keeping the test panel in relative humidity i.e. C, D. What was applied was wetting the test panel in cycle A, which works on continuous run operating mode with 18 min of wetting time and 102 min of dry period. The relative humidity during dry period is 40 to 60%. The specimen will have difference in color appearance and physical property when lasted to 1000 hours. Using Spectrophotometer color difference of test panel is calculated. The used is Q-SUN Xe-3 from Q-lab shown in figure 3.9 [38] [40].

Figure 3.9- Q-Panel Lab Products QSUN.

3.13 Test for tackiness

Test works on visual observation and called as blocking test done after tannin test. It is performed by arranging a lab scale setup of pilling up cork sheets in oven for 24 hours at 50ºC temperature. In storage it involves lining up cork sheets one on other in a row after coated with primer paint, results in primer painted on cork sheet adhere to the back of the other cork sheet which was lied on top of it. This was the problem when sheets are piled up in line, while storing in the industry. To avoid this problem, a lab setup of cutting two equally painted cork sheets piled one upon other with additional weight of 300grams over it in an oven for 50ºC and observed after 24 hours. The test concludes on less tackiness of the cork sheets after applying primer paint on it. With reference to the gloss meter reading, the results are verified to see the matt appearance of the paint, as more the coat is matt less is the tackiness.

3.14 Climatic chamber test

This test is to see the effects on cork panel to accelerate the migration of tannins by placing the samples in a high humidity and temperature. Cork panels are kept for 2 weeks (336 hours) in the chamber which has temperature 60ºC and humidity 95%, control with lighting effect from 0- 24 hours (2 period lights on and 2 periods lights off). The observations are made weather the tannins appear during this span of time. The stability of tannins in artificial aging and storage, when kept in this condition weather, are assassed. The model used for testing was TK 120 from NUVE (figure 3.10).

Figure 3.10- NUVE TK120 for Climatic chamber test

3.15 Solubility test

To perform the tannins solubility test, a specific area with 2x2 cm of cork sheet should be cut and immerge in a glass crucible filled with 10 ml of the selected solvent or co-solvent. The visual alterations of the solution, and also of the raw material, with time should be registered along 1 to 3 days

4 Results and discussion

4.1 Study on different strategies to block tannins

The elements that have an important role in the formulation in mill base as well as in thinning of mill base, were categorized in four different phases (1- Solvent characterization; 2-Characterization of Resin; 3-Anti-tannins additives selection; 4-Filler/extender selection) and presented in an explanatory diagram (Figure 4.1). This diagram represents the general formulation for manufacturing the paint. In each phase, various sets of tests were performed, namely Viscosity, Settling, Opacity, Gloss, Test for tackiness, Adhesion to PVC and cork, Tannin test, QUV and QSUN, Rheology test.

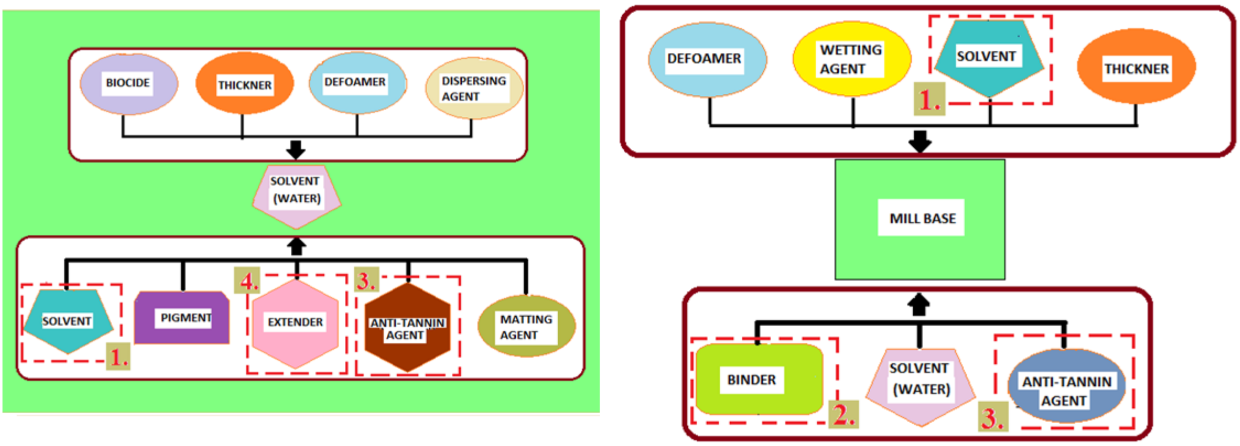

Figure 4.1- Different strategies to block tannins in mill base and thinning process.

To reach the set objective of this project (figure 4.2), the parameters presented in table 4.1 should be fulfilled. The attained results of each test performed in the several optimization phases (1- Solvent characterization; 2-Characterization of Resin; 3-Anti-tannins additives selection; 4-Filler selection) were compared with the desired parameter results.

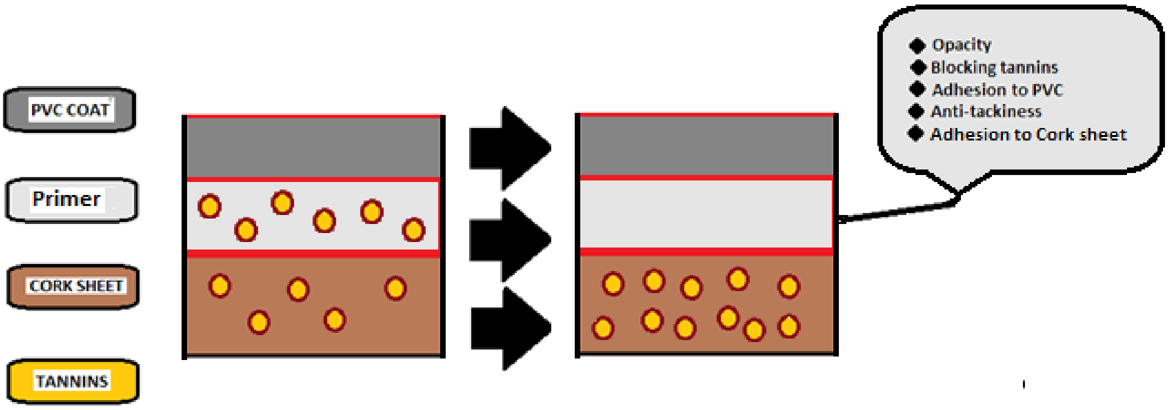

Figure 4.2- Pictorial graphic for the needed parameters required for anti-tannin primer

Table 4.1- Parameter result specification for anti-blocking primer.

Tests		Notations	Results
Viscosity (CF4)		Seconds	20-30
pH		-	6-7
Settling		Yes/No	No
Opacity		%	80-90
	20º		>2
Gloss	**60º**	Gloss Units (GU)	>5
	85º		>10
Adhesion to PVC		Yes/No/Inconclusive	Yes
Blocking		Yes/No/Inconclusive	Yes
Adhesion to cork		Class: 0 to 5	0
Tannin test		Yes/No/Inconclusive	Yes
Climatic chamber test		Yes/No/Inconclusive	Yes

4.2 Solvent characterization

In the formulation of water-based products, it is common to use co-solvents (or coalescing agents). This are filmification agents that help the resin to filmificate properly. There are various co-solvents used in a paint industry, being the most commonly applied texanol, glycols, isopropanol, white sprit etc. The objective it is verify the solubility of tannins in different co-solvents and compare the attained results among them for selecting the co-solvent with the best properties.

Solvent characterization is performed using two tests, solubility of tannin in co-solvent and solubility of tannin in water using different pH. Nine co-solvents were selected for the solubility test (figure 4.3). pH test was performed by using water at various pH (4; 6; 8; 10) and check the solubility of tannins at each value.

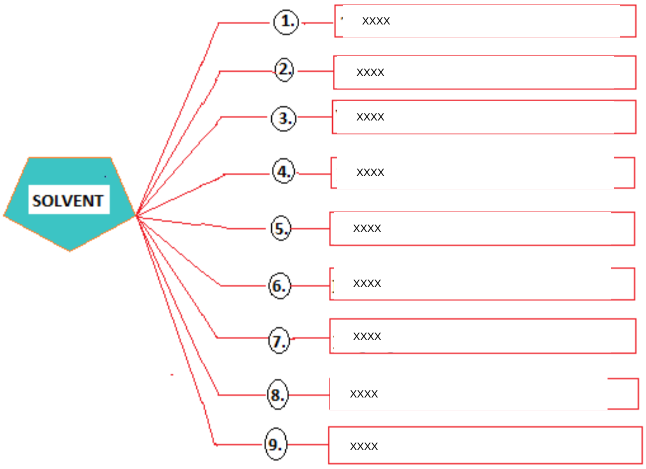

Figure 4.3- Tested solvents.

4.2.1 Solubility of tannin in co-solvent

After 1 to 3 days, it can be observed that if tannins are soluble in any of the solvent, color changes to brown or light brown will be observed (table 4.2). The solvents with good results are XXXX, XXXX, and XXXX, no change in color and no tannins seem to be present. In the other assays, various observations can be seen. XXXX was vaporized leaving no sample in crucible; XXXX sample showed difference in color turning into brown. The solvents, such as XXXX, XXXX and XXXX exhibit a similar behavior by turning the clear solvent into light brown color where tannins are slightly soluble. White spirit did not have color change, but it is a flammable liquid and vapor. According to this test, the best solvents, i.e. XXXX, XXXX and XXXX can be used in the subsequent formulation and tested for binders, anti-tannin agent and extenders.

Table 4.2- Results for solubility test of cork in the tested solvent.

Name	Picture (before)	Picture (after)	Picture (after)
XXXX			
XXXX			
XXXX			
XXXX			
XXXX			
XXXX			
XXXX			
XXXX			
XXXX			

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4.2.2 Solubility of tannin in water of different pH

This test shows the importance of pH in attaining the goal of this project. After 1 to 3 days (table 4.3), it can be observed that tannins are soluble in water having high pH i.e. 8 and 10, as color changes to brown or light brown. The water having pH 4 and 6 results promotes less solubility of tannins. In the following formulation that is to be tested for binders, anti-tannin agent and extenders should maintain at pH between 4-6.

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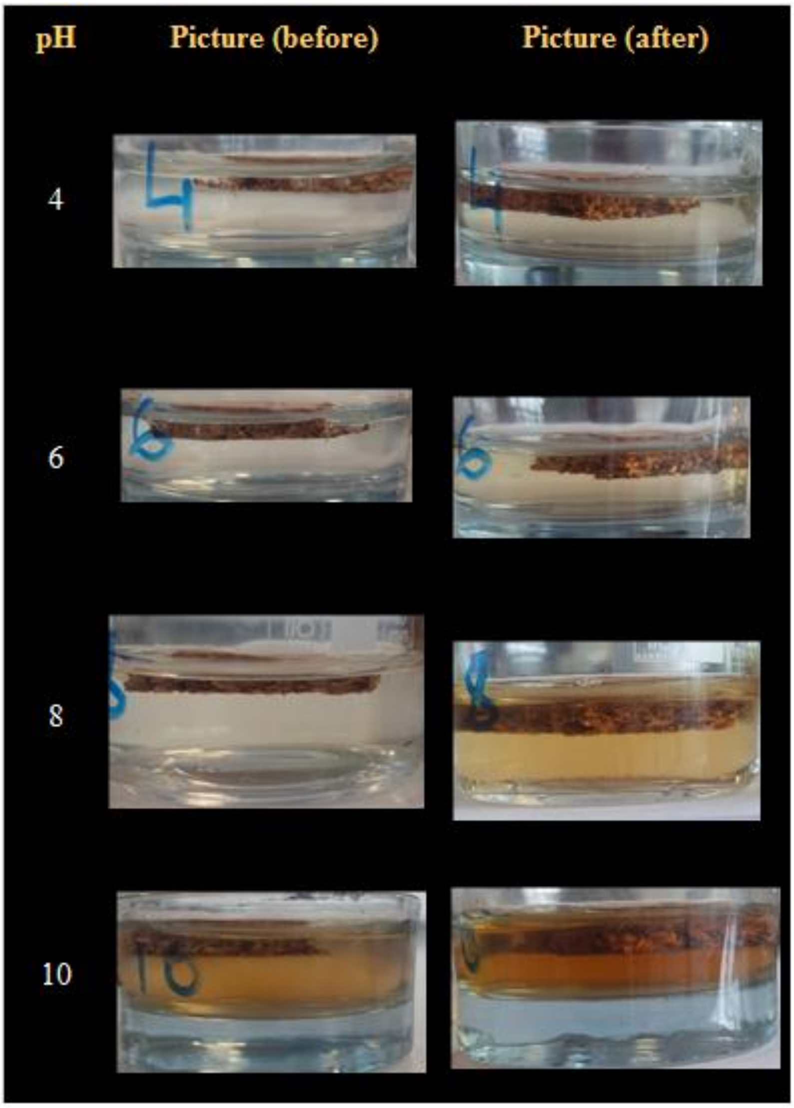
Table 4.3- Results for solubility test of cork in water at different pH (4, 6, 8, 10).



4.3 Characterization of Resin

The used resins are differentiated based on the chemical type, ionic character, solids content and pH (Table 4.4). It is also based on manufacturing process shown in Figures 4.4 and 4.5 The resin sub-groups are:

- XXXX(R1-R6).
- XXXX (S1).
- XXXX (V1).
- XXXX (O1).
- XXXX (C1).
- XXXX (A1.1 & A1.2).

Resins (Table 4.4) subtype of conventional resin was composed by six XXXX (water-based resins; R1 to R6) also called XXXX. Another subtype constituted in a XXXX resin (S1), which is XXXX resin used as a co-binder for water-borne paints with XXXX act as a major difference among other resins; other subtypes was XXXX (V1) a plasticizer-free aqueous XXXX (O1). More two subtypes of resins were assessed and included a XXXX resin (C1) and two XXXX resin (A1.1 and A1.2). The XXXX resin contains a water-based XXXX and XXXX, while XXXX.

Table 4.4- Classification of resin and its properties.

Resin	Ionic character	Chemical type	Manufacturing process	pH	Solid content (%)
R1	XXXX	XXXX	1	8.0-9.0	46.5
R2	XXXX	XXXX	1	8.5-9.5	40.0
R3	XXXX	XXXX	1	4.7	42.5
R4	XXXX	XXXX	1	7.0-8.0	45.5
R5	XXXX	XXXX	1	7.0-9.0	41-43
R6	XXXX	XXXX	1	7.3-7.9	42.3
S1	XXXX	XXXX	1	8.0-9.0	98-99
O1	XXXX	XXXX	1	8.0	40.0
V1	XXXX	XXXX	1	4.0-5.0	54-56
C1	XXXX	XXXX	2	4.0-5.0	45.0
A1.1	XXXX	XXXX	2	6.5-7.5	55.0
A1.2	XXXX	XXXX	2	7.0	40.0

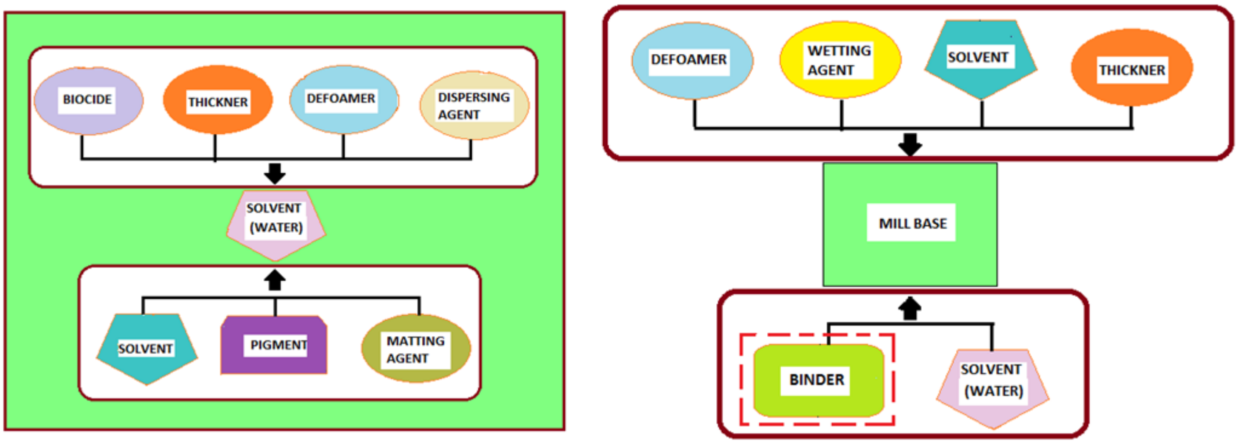


Figure 4.4- Manufacturing process 1 with mill base and thinning process used for characterization of the resin.

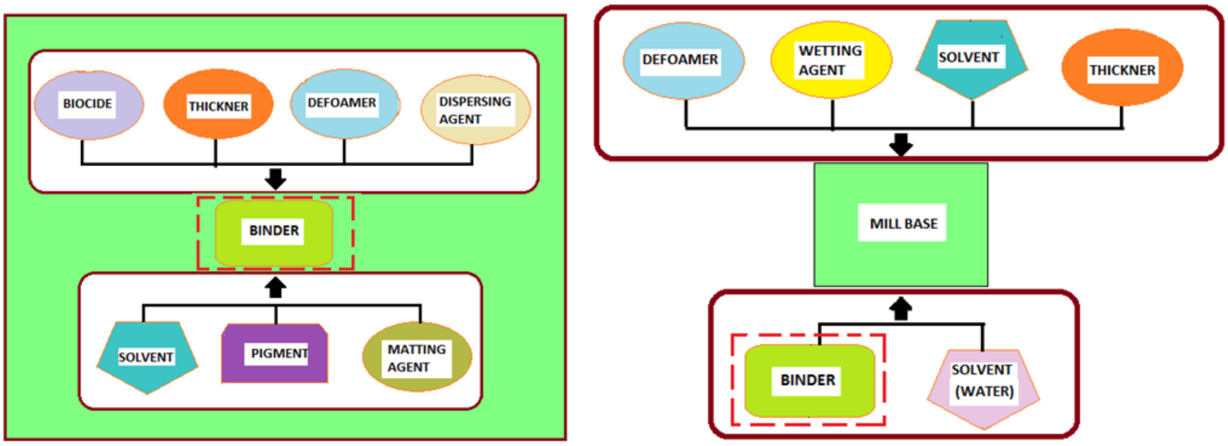


Figure 4.5- Manufacturing process 2 with mill base and thinning process used for characterization of the resin.

Nine of the 12 tested resins were XXXX and high-quality stain-blocking property for wood, because it is much more common wood than cork as a construction material. But cork has much more tannins than wood. That is why a good resin for wood will help in blocking tannin in cork.

Using the resin in the formulation, topcoat primer was generated and several test (Part 1- Viscosity, pH, Settling, Opacity, Gloss; Part 2- Adhesion to PVC, Test for tackiness, Adhesion to cork; Part 3- Tannin test; Part 4-QUV, QSUN; Part 5- Rheology test) were performed, which results are then discussed.

4.3.1 Part 1- Viscosity, Settling, Opacity, Gloss

The table 4.5 shows the results of the evaluated resins. Viscosity and stability are maintained, which are crucial for storage to long periods. Stability is seen by checking the viscosity after completion of the formulation and then comparing the reached viscosity after 1 week. If the difference in viscosity is large, a problem of stability will occur unless less difference can be resolved by improvising the formulation at the final. The stability period of these samples was two months and viscosity was checked once a week. The same period was applied for test of settling, but R2 and R3 failed.

Table 4.5- Results of Part 1- Viscosity, pH, Settling, Opacity, Gloss for characterization of the resin.

Resin	Viscosity Stability		pH	Settling	Opacity	Gloss		
	Viscosity (CF4)	Stable				20º	60º	85º
R1	30	Yes	8.3	No	93.5	2.4	12.8	24.0
R2	23	Yes	8.7	Yes	90.4	3.4	21.3	42.2
R3	20	Yes	5.0	Yes	86.1	3.0	16.4	25.5
R4	25	Yes	8.0	No	81.2	1.4	5.3	14.9
R5	20	Yes	7.6	No	91.0	1.9	9.6	22.8
R6	34	Yes	7.5	No	91.2	2.5	14.6	33.0
S1	29	Yes	7.0	No	85.8	20.2	63.9	93.2
V1	32	Yes	8.0	No	92.9	5.5	28.9	47.2
O1	23	Yes	8.2	No	92.6	2.5	15.1	30.8
C1	32	Yes	5.0	No	89.8	2.4	12.1	22.5
A1.1	33	Yes	6.0	No	89.5	3.7	19.1	21.0
A1.2	29	Yes	6.2	No	91.6	2.3	10.7	19.5

As per the pH test (Table 4.5), it is concluded that it is mandatory to work with a system of pH as low as possible; pH must be maintained between 6-7. R3, S1, C1, A1 and A2 originated appropriate results, whereas other resins fell short and some far higher. Satisfactory results of opacity and gloss were observed for all.

4.3.2 Part 2- Test for tackiness, Adhesion to PVC and cork

XXXX resins mostly failed to pass the adhesion test to PVC and blocking (Table 4.6). R5 and V1 passed the test for tackiness fulfilling the objective directly without addition of additives. S1 and A1 required more time for drying, which cannot be solved. The resins, other than conventional, showed good adhesion to PVC without any additive. All resin-based primer has good adhesion to the cork.

Table 4.6- Results of Part 2- Test for tackiness, Adhesion to PVC and cork for Characterize Resin.

Resin	Adhesion to PVC	Blocking	Adhesion to cork
R1	Inconclusive	Fail	0
R2	Fail	Fail	0
R3	Inconclusive	Fail	0
R4	Fail	Fail	0
R5	Fail	Pass	0
R6	Fail	Fail	0
S1	Pass	Fail	0
V1	Pass	Pass	0
O1	Pass	Fail	0
C1	Pass	Fail	0
A1.1	Pass	Fail	0
A1.2	Pass	Fail	0

4.3.3 Part 3- Tannin test

Similar results (Table 4.7 and 4.8) were attained by conventional resins during the tannin test proving that this subtype of resin does not show anti-tannin property to produce a primer, unless anti-tannin additives are included. S1 and A1 originated good results but overall failed due to another parameter (i.e the test for tackiness). Resins C1 and V1 showed appropriate results among all and can directly be selected for the final formulation, in which the primer is reformulated to improve parameters. A2 resin resulted in a suitable blocking tannin primer except for tackiness, which, after further formulation to reduce tackiness, increased the migration of tannin on top coat of a primer. Thus, A2 failed the tannin test.

Table 4.7- Results of Part 3- Tannin test for characterization of resins: R1, R2, R3, R5, R6, and S1.

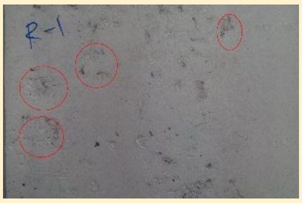
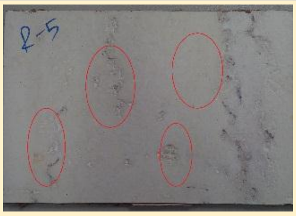
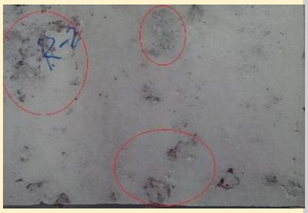
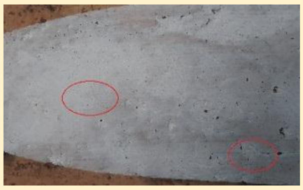
Resin	Tannin test	Visual	Resin	Tannin test	Visual
R1	Fail		**R5**	Fail	
R2	Fail		**R6**	Fail	
R3	Fail		**S1**	Inconclusive	

Table 4.8- Results of Part 3- Tannin test for characterization of resins: R4, V1, O1, A1.1, A1.2, and C1.

Resin	Tannin test	Visual	Resin	Tannin test	Visual
R4	Fail		**V1**	Inconclusive	
O1	Fail		**A1.1**	Pass	
C1	Pass		**A1.2**	Pass	

4.3.4 Part4- QUV and QSUN

When a paint is subjected to QUV and QSUN tests, it is expected that the color properties will vary with time. So, control color which are visible to the naked eye and are difficult to keep constant in the weather were selected. In these tests, the ΔE* should be as minimum as possible.

The color variations (at t=0 and 1000 hours) occurring during the accelerated aging test are presented for each of the resins (Table 4.9 and figures 4.6 and 4.7). Looking at the L*a*b* values for each resin, it can objectively determined that most of sample don't match in color. These values tell us that resin sample is lighter or darker, redder or greener and yellower or bluer after test. All resins except S1 is lighter with ΔL* value of 2.8; the rest of them are less dark with less ΔL* values. There is almost no change in Δa* beside S1. Δb* values display only more yellowness in S1, R2 and O1 i.e. 2.1 and 4.2. S1 reduced yellowness after the test. Overall, the color difference between the resins R1,R3, R4, R5, R6, V1, C1, A1 and A2 is less with lower value of ΔE*. Higher color difference was obtained in R2, S1 and O1. Other resins have minimum color difference and are suitable for QUV conditions.

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Table 4.9- Results from QUV.

Resin	Before L*	After L*	ΔL*	Before a*	After a*	Δa*	Before b*	After b*	Δb*	ΔE*
R1	97.2	96.7	↓ -0.5	-0.9	-0.8	↑ -0.1	0.0	0.2	↑ 0.2	0.6
R2	96.4	95.5	↓ -0.9	-1.0	-1.2	↓ 0.2	0.3	2.5	↑ 2.1	2.3
R3	94.5	93.0	↓ -1.5	-0.8	-0.8	0.0	0.6	0.4	↓ -0.2	1.5
R4	92.4	92.3	↓ -0.1	-1.1	-1.1	0.0	-0.2	0.0	↓ -0.2	0.2
R5	96.1	95.8	↓ -0.3	-1.0	-1.0	0.0	0.1	0.5	↑ 0.3	0.5
R6	96.3	95.9	↓ -0.4	-1.0	-1.0	0.0	0.1	0.2	↑ 0.1	0.4
S1	88.6	91.3	↑ 2.8	-3.4	-1.3	↑ -2.1	10.4	7.8	↓ -2.6	4.3
O1	96.9	94.0	↓ -2.9	-1.0	-0.8	↑ -0.2	1.1	5.2	↑ 4.2	5.1
V1	97.3	96.8	↓ -0.5	-1.0	-0.9	↓ -0.1	0.2	0.5	↑ 0.3	0.6
C1	96.5	95.7	↓ -0.9	-0.9	-0.8	↓ -0.1	0.4	1.4	↑ 1.0	1.3
A1	95.5	95.5	0.0	-1.1	-1.0	↓ -0.1	-0.4	0.0	↓ -0.4	0.4
A2	96.3	95.6	↓ -0.7	-1.0	-1.0	0.0	0.4	0.7	↑ 0.3	0.8

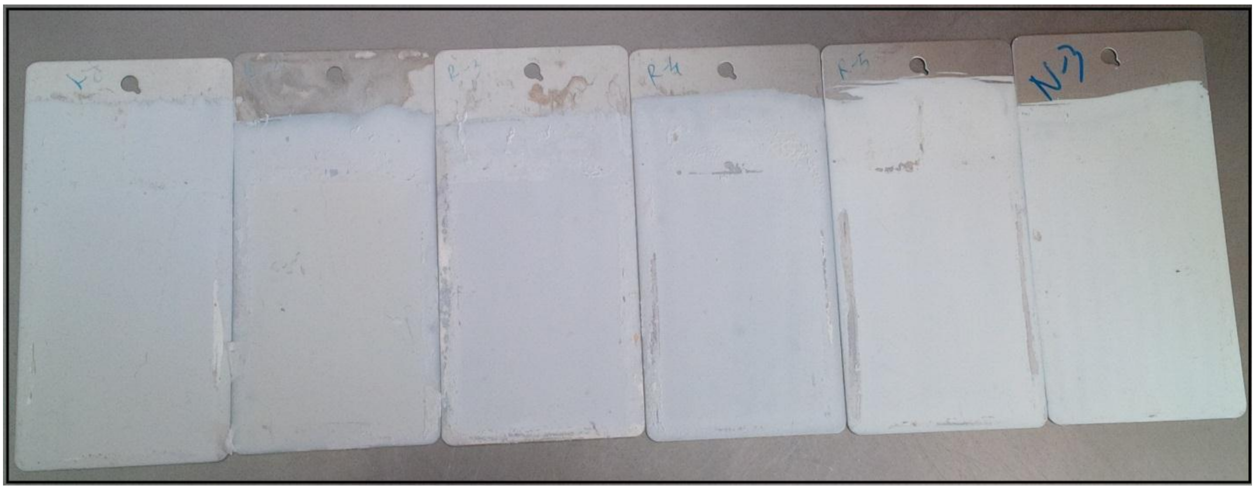

Figure 4.6- Test panels for R1-R6 of QUV after 1000 hours.

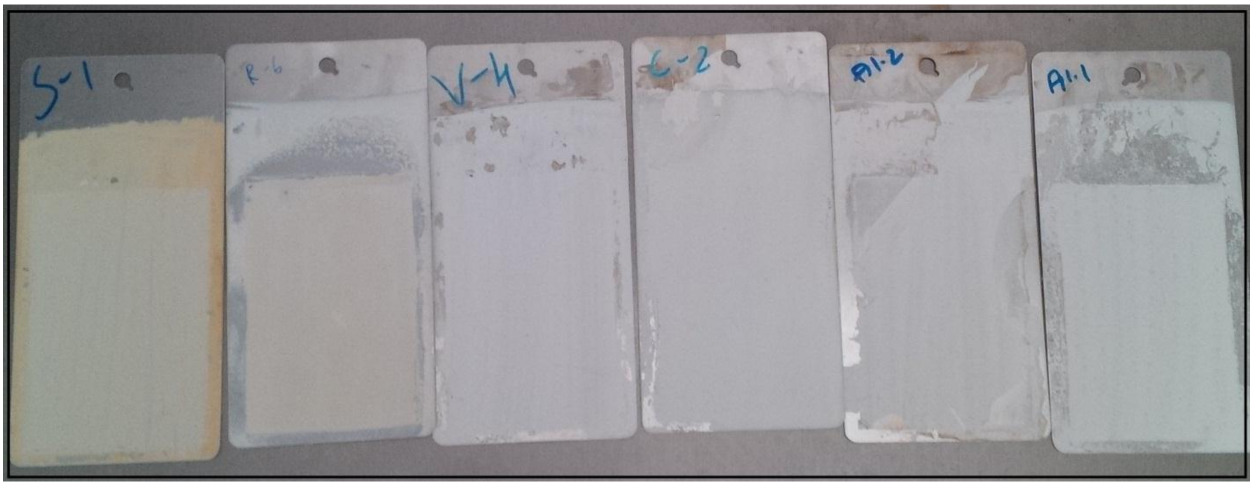

Figure 4.7- Test panels for S1, O1, V1, C1, A1.1 and A1.2 of QUV after 1000 hours.

Table 4.10 observes the difference in QSUN test performance with colorimetric properties of each resin. Looking at the L*a*b* values for each resin and calculating ΔL*, Δa*, and Δb* in which ΔL* results in showing less darkness after the test except R3 being darker than all. S1 values (ΔL*= 2.8) is lighter from all. Nearly every resin has no difference change in Δa* value. S1 depleted the yellowness after the test and overall being the resin which has higher ΔE* value i.e. more color difference among all resins. All resins passed this test with having minimum color difference value with exception of R3 and S1.

O1 resin was washed out after 100 hours and cannot be further proceeded due no availability of material on the test panel. The test panels after 1000 hours in QSUN chamber are shown in figures 4.8 and 4.9.

Table 4.10- Results from QSUN.

Resin	Before L*	After L*	ΔL*	Before a*	After a*	Δa*	Before b*	After b*	Δb*	ΔE*
R1	95.2	94.2	↓ -1.0	-1.1	-1.1	0.0	-1.1	-1.0	↑ -0.1	1.0
R2	95.5	94.9	↓ -0.6	-1.1	-1.3	↑ 0.2	-1.1	0.9	↑ -0.2	0.7
R3	92.6	90.3	↓ -2.2	-0.9	-0.9	0.0	0.3	0.2	↓ -0.1	2.2
R4	92.1	91.7	↓ -0.4	-1.3	-1.2	0.0	-0.5	-0.9	↑ 0.4	0.6
R5	96.1	96.0	↓ -0.2	-1.0	-1.0	0.0	0.1	0.1	0.0	0.2
R6	96.0	95.5	↓ -0.6	-1.1	-1.0	↓ -0.1	-0.1	-0.2	↑ 0.1	0.6
S1	88.6	91.4	↑ 2.8	-3.3	-1.2	↓ -2.1	9.2	2.4	↓ -6.8	7.7
O1				Material not present						
V1	97.1	96.6	↓ -0.5	-1.0	-1.0	0.0	0.0	-0.1	↓ -0.1	0.5
C1	96.4	95.7	↓ -0.7	-0.9	-0.9	0.0	0.4	0.5	↑ 0.1	0.7
A1	96.0	94.9	↓ -1.1	-1.1	-1.2	↑ 0.1	-0.3	-0.4	↑ 0.1	1.1
A2	95.9	95.2	↓ -0.7	-1.1	-1.1	0.0	-0.7	-0.7	0.0	0.7

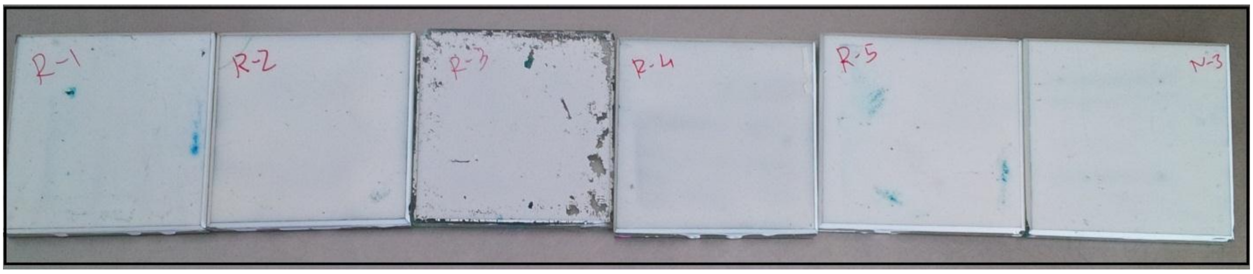

Figure 4.8- Test panels of R1-R6 of QSUN after 1000 hours.

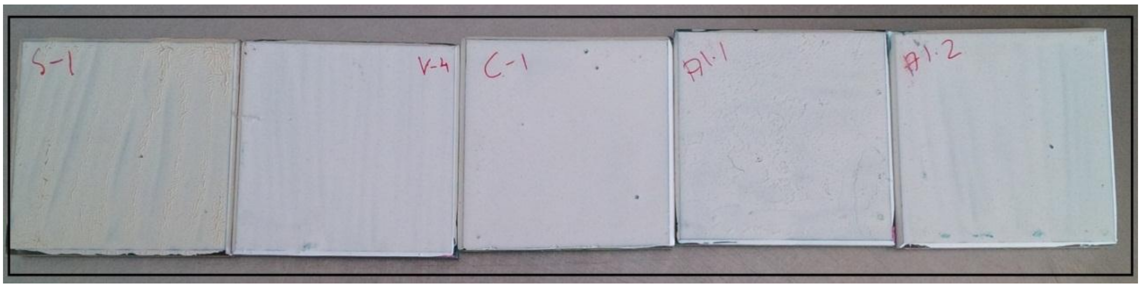

Figure 4.9- Test panels of S1, O1, V1, C1, A1.1, and A1.2 of QSUN after 1000 hours.

4.3.5 Part 5- Rheology test

Flow curve

In this test, the viscosity of the fluid is verified according to the cut-off rate provided to it. The discussion of these graphs will have a greater focus at lower cut rates because one of the problems that paints may have is sedimentation. The best formulations will be

those with higher viscosity at lower shear rates and lower viscosity at higher shear rates and also a Newtonian profile. The results are exhibited in Figure 4.10 and 4.11.
Resins R2, R3, C1, A1.1 and O1 presented a curve which best matches the goal having a profile slightly downward Newtonian. It can be also noted that these resins have higher viscosity at low shear rates and lower viscosity at higher shear. The resin R6 exhibited the highest viscosity at low shear rates, and followed by S1, R4, R1 and V1, with reduced viscosity at lower shear rate and lower viscosity at higher strain rate. The best formulation was reached with R2, R3, C1, A1.1 and O1.

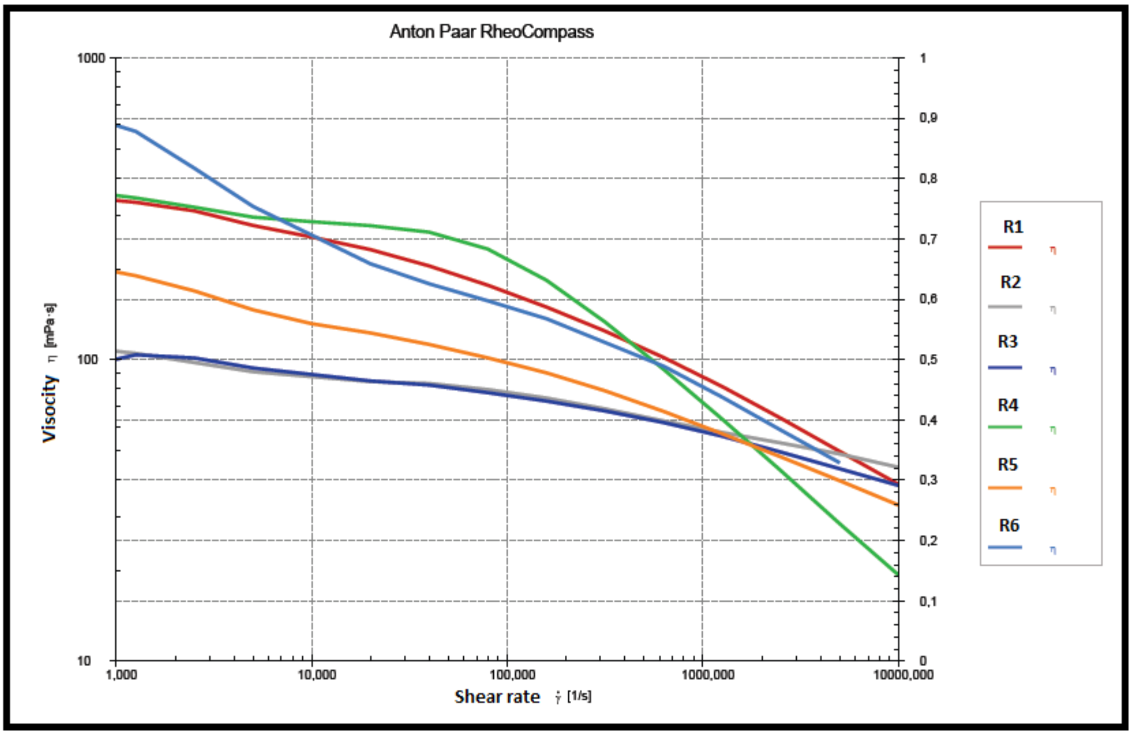

Figure 4.10 Flow curve for resin R1-R6

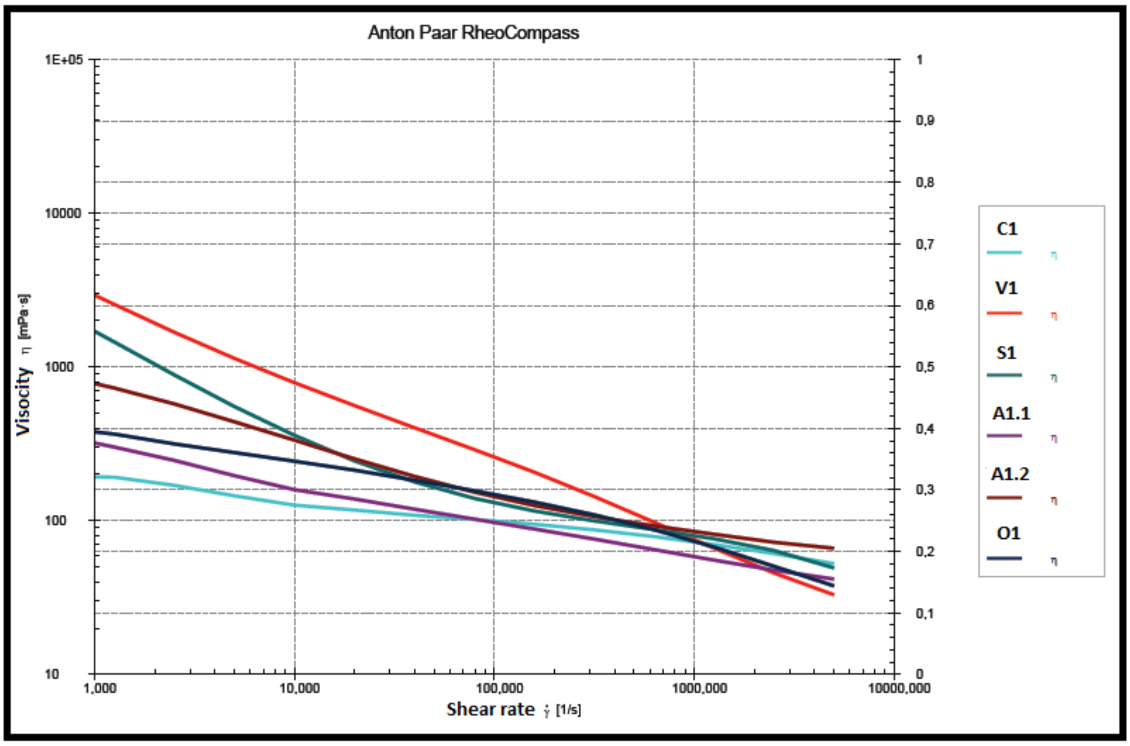

Figure 4.11 Flow curve for resin C1, V1, S1, A1.1, A1.2 and O1.

4.4 Effect of special anti-tannins additive on resin

Since several resins failed to display tannin blocking property with suitable other characteristics, the work proceeded with some reformulations of conventional resins by incorporating anti-tannin additives in order to establish some improvements in the primers, which failed the primary objective. Two different type of additives were used, a liquid additive i.e. XXXX and a filler called 'XXXX'. Subsequently new tests (Part 1-Viscosity, pH, Settling, Opacity, Gloss; Part 2-Adhesion to PVC, Test for tackiness, Adhesion to cork; Part 3- Tannin test) were performed, which results are discussed below.

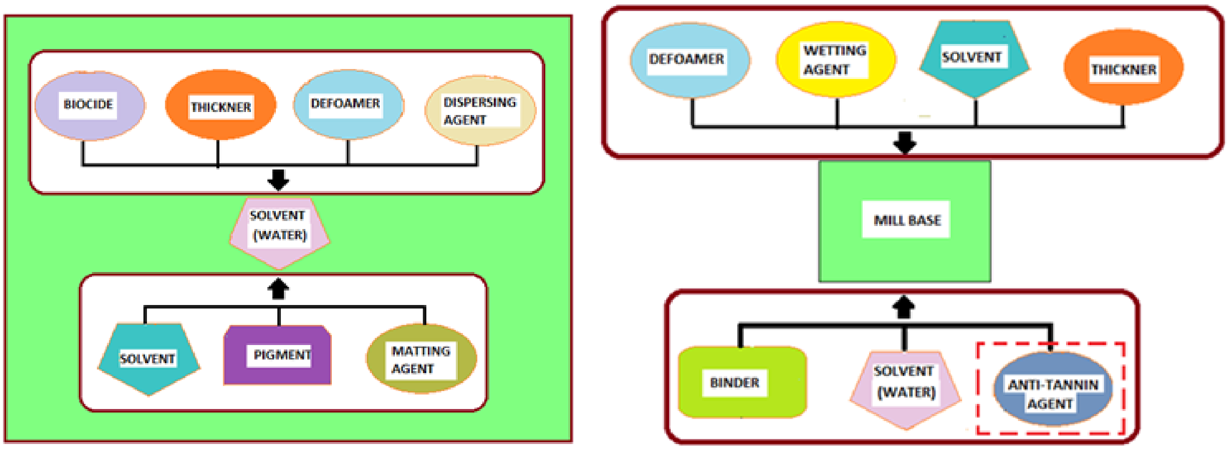

Figure 4.12- Mill base and thinning process used with special anti-tannins additive i.e. liquid additive.

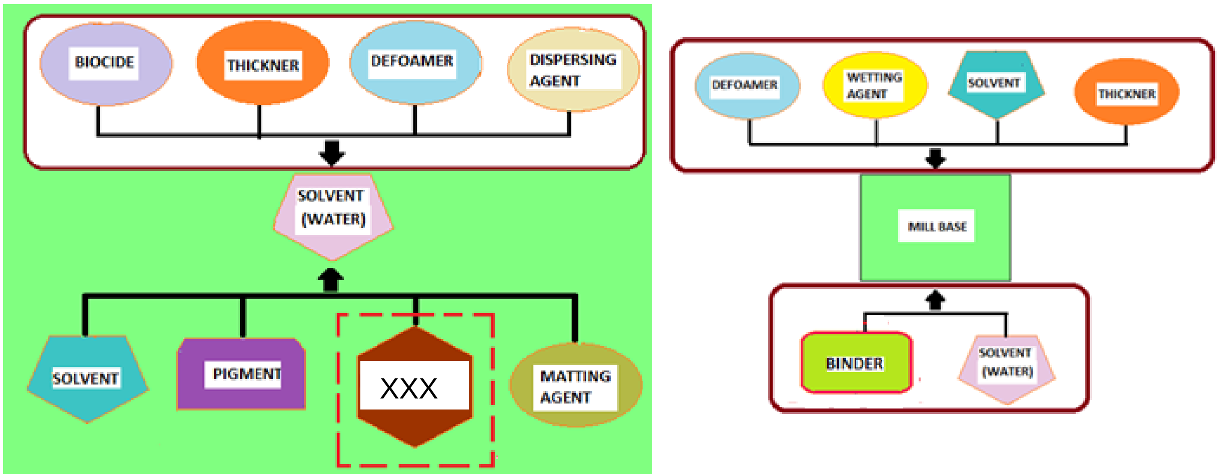

Figure 4.13- Mill base and thinning process used with special anti-tannins additive i.e. XXXX.

4.4.1 Part 1- Viscosity, Settling, Opacity, Gloss

The attained results of both formulations using liquid additive and XXXX are presented in Table 4.11 and 4.12. There is no difference in the viscosity and also in stability except with the pH, which made no difference in the formulation apart from that there is an increase in the pH of all resins in both cases. The primer using R3 resin resulted in solidification due to addition of the liquid additive, demonstrating that this additive is not compatible with R3. The settling problem can be seen in both R2 based formulations using liquid additive and XXXX. The same problem was observed for R5 resin only when the formulation contained XXXX. The changes found in opacity and gloss can be neglected at this stage and be taken into consideration only after formulating the primer.

Table 4.11- Results of Part 1- Viscosity, pH, Settling, Opacity, Gloss for special anti-tannins additive i.e. liquid additive

Resin	Viscosity Stability		pH	Settling	Opacity	Gloss		
	Viscosity (CF4)	Stable				20º	60º	85º
R1	20	Yes	8.6	No	93.4	2.0	9.5	20.5
R2	30	Yes	8.9	Yes	87.9	2.0	9.7	21.8
R3	Fail (Not stable)							
R4	20	Yes	8.8	No	92.3	2.4	12.4	24.4
R5	18	Yes	8.6	No	92.8	2.0	8.7	23.2

Table 4.12- Results of Part 1- Viscosity, pH, Settling, Opacity, Gloss for special anti-tannins additive i.e. XXXX.

Resin	Viscosity Stability		pH	Settling	Opacity	Gloss		
	Viscosity (CF4)	Stable				20º	60º	85º
R1	28	Yes	8.5	No	93.7	2.0	8.5	19.2
R2	20	Yes	8.7	Yes	89.7	1.8	8.8	26.3
R3	30	Yes	6.5	No	91.9	2.4	13	35.8
R4	31	Yes	8.4	No	95.1	2.0	9.3	22.9
R5	20	Yes	8.0	Yes	94.0	1.9	8.7	26.3

4.4.2 Part 2- Test for tackiness, Adhesion to PVC and cork

Further tests performed with conventional resins and the selected additives are presented in Tables 4.13 and 4.14. No significant enhancements were detected except for R5 as being consistent in showing less tackiness. R1 displayed good adhesion to PVC only with XXXX.

Table 4.13- Results of Part 2- Test for tackiness, Adhesion to PVC and cork for special anti-tannins additive i.e. liquid additive.

Resin	Adhesion to PVC	Blocking	Adhesion to cork
R1	Inconclusive	Fail	0
R2	Fail	Fail	0
R3	Fail (Not stable)		
R4	Fail	Fail	0
R5	Inconclusive	Pass	0

Table 4.14- Results of Part 2- Test for tackiness, Adhesion to PVC and cork for special anti-tannins additive i.e. XXXX.

Resin	Adhesion to PVC	Blocking	Adhesion to cork
R1	Pass	Fail	0
R2	Fail	Fail	0
R3	Inconclusive	Fail	0
R4	Fail	Fail	0
R5	Inconclusive	Pass	0

4.4.3 Part 3- Tannin test

Using the liquid additive, no significant effect was perceived in conventional resins performance except for R5, which neglects the possibility of choosing liquid additive as an anti-tannin additive for the final formulation (table 4.15).

Table 4.15- Results of Part 3- Tannin test for special anti-tannins additive (liquid additive).

Resin	Tannin test	Visual	Resin	Tannin test	Visual
R1	**Fail**		**R4**	**Fail**	
R2	**Fail**		**R5**	**Pass**	
R3	**Fail**				

XXXX (table 4.16) gave appropriate anti-tannin characteristics for R1 and R3, which was further included in the final selection for increase in Tackiness. R2, R4, and R5 resins failed in this final prospect, and were not considered due to their low chances of producing a primer with good performance.

Table 4.16- Results of Part 3- Tannin test for special anti-tannins additive (XXXX).

Resin	Tannin test	Visual	Resin	Tannin test	Visual
R1	Pass		R4	Fail	
R2	Fail		R5	Fail	
R3	Pass				

4.5 Effect of fillers on resin.

The influence of fillers in blocking tannin and establishing some different properties, which are needed for the formulation, was evaluated. The new formulations (Figure 4.14 and 4.15) were prepared based on R6 and 8 different fillers which are different in chemistry and physical properties. The fillers chosen have low pH values. Besides blocking tannin, the objective is to select filler which produce a formulation primer with low pH. In the previous phases (resin characterization and Anti-tannin agent selection), no change in gloss was seen, but addition of fillers can make a difference to reduce gloss. After completion of the formulations, new tests (Part 1 Viscosity, pH, Settling, Opacity, Gloss; Part 2-Adhesion to PVC, Test for tackiness, Adhesion to cork; Part 3- Tannin test) were performed, which results are discussed below.

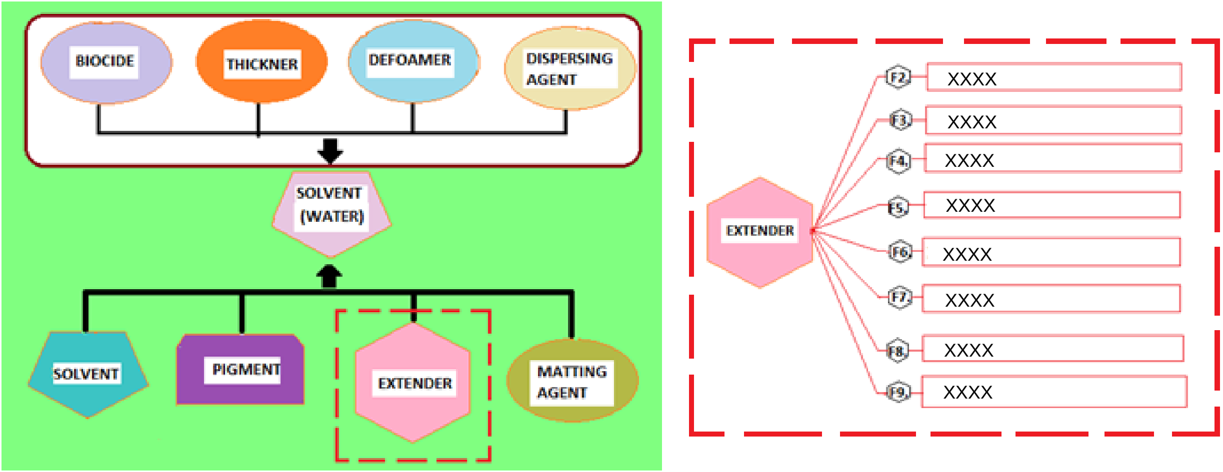

Figure 4.14- Mill base process used with filler and classification of fillers used in this phase.

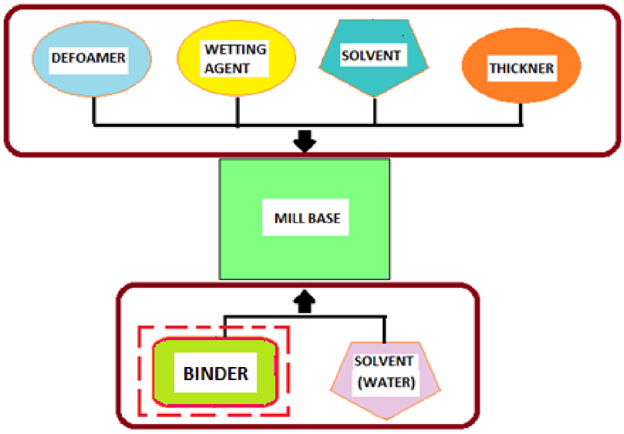

Figure 4.15- Thinning process used with fillers.

4.5.1 Part 1- Viscosity, Settling, Opacity, Gloss

The attained results (Table 4.17) indicated that viscosity was maintained except for F4 and F6, which also showed a problem of settling. Filler F2 demonstrated the problem of settling even the viscosity being stable.

Opacity decreased as almost falling into the requested range (80-90). The opacity of F3 and F6 falled way less and did not match to the range. Improvement can be seen in overall final primer when any fillers is used in the formulation. Fillers are responsible in maintaining the pH. The measured pH also was in the range, and the value was almost equal for all, except for F9 which is the lowest.

Gloss is measured in different angles (by which the test of tackiness is dependent), but considering 85 degree (matt finish) as an important reading, F3, F4, F5 and F6 have lower values (5.5-8.9), and the others (F2, F7, F8, F9) have significantly higher values (20.2-28.3).

Table 4.17- Results of Part 1- Viscosity, pH, Settling, Opacity, Gloss for fillers.

Fillers	Viscosity Stability		pH	Settling	Opacity	Gloss		
	Viscosity (CF4)	Stable				20º	60º	85º
F2	32	Yes	7.6	Yes	83.5	1.6	5.9	20.2
F3	32	Yes	7.5	No	60.0	1.4	4.2	5.5
F4	34	No	7.7	Yes	86.8	1.7	5.6	7.8
F5	23	Yes	7.5	No	84.7	1.6	5.4	8.8
F6	35	No	7.7	Yes	76.3	1.6	5.4	8.9
F7	32	Yes	7.6	No	82.1	1.8	8.3	25.2
F8	31	Yes	7.7	No	84.4	2.0	0.1	26.0
F9	25	Yes	7.0	No	90.6	1.5	6.6	28.3

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4.5.2 Part 2- Test for tackiness, Adhesion to PVC and cork

All fillers show good blocking property (Table 4.18), however no adhesion to PVC was detected. The results of the tackiness test are in accordance with the gloss tests.

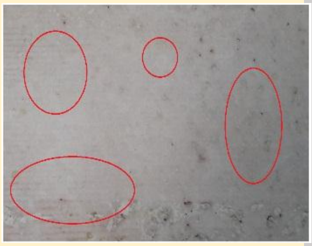
Table 4.18- Results of Part 2- Test for tackiness, Adhesion to PVC and cork for fillers.

Fillers	Adhesion to PVC	Blocking	Adhesion to cork
F2	Fail	Pass	0
F3	Fail	Pass	0
F4	Fail	Pass	0
F5	Inconclusive	Pass	0
F6	Fail	Pass	0
F7	Fail	Pass	0
F8	Fail	Pass	0
F9	Fail	Pass	0

4.5.3 Part 3- Tannin test

The resulst of the tannin test are shown in table 4.19. It can be concluded that fillers are not responsible by blocking tannin. The F9 outcomes are the best among all since it originated a primer of low pH and less tackiness, thus it was choosen for the final formulation.

Table 4.19- Results of Part 3- Tannin test for fillers.

Fillers	Tannin test	Visual	Fillers	Tannin test	Visual
F2	Fail		**F6**	Fail	
F3	Fail		**F7**	Fail	
F4	Fail		**F8**	Fail	
F5	Fail		**F9**	Fail	

4.5.4 Part 4- Rheology test

Flow curve

Each one of the filler, except F3 and F9, matches the desire behavior with a profile slightly downward Newtonian and higher viscosity at lower shear rates, as well as lower viscosity at higher shear rates (Figure 4.16 and 4.17). The higher viscosity at low shear rates and lower viscosity at the higher strain rates was exhibited by F9. F3 changed to lowest viscosity at lower shear rate.

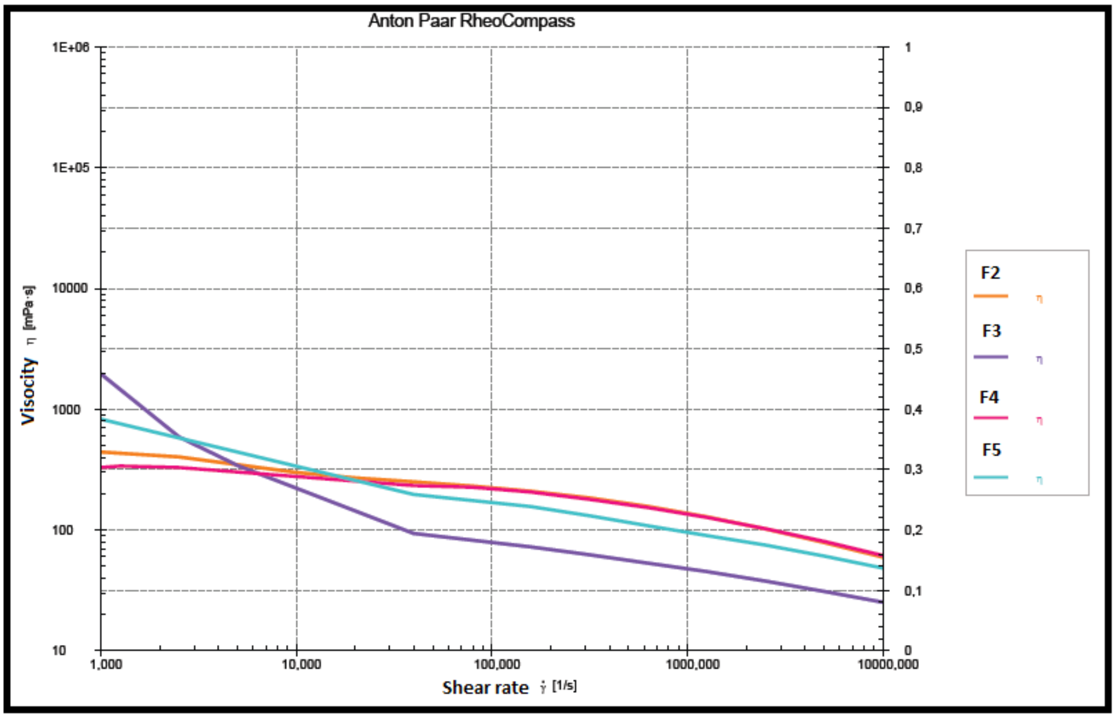


Figure 4.16- Flow curve for fillers F2-F6

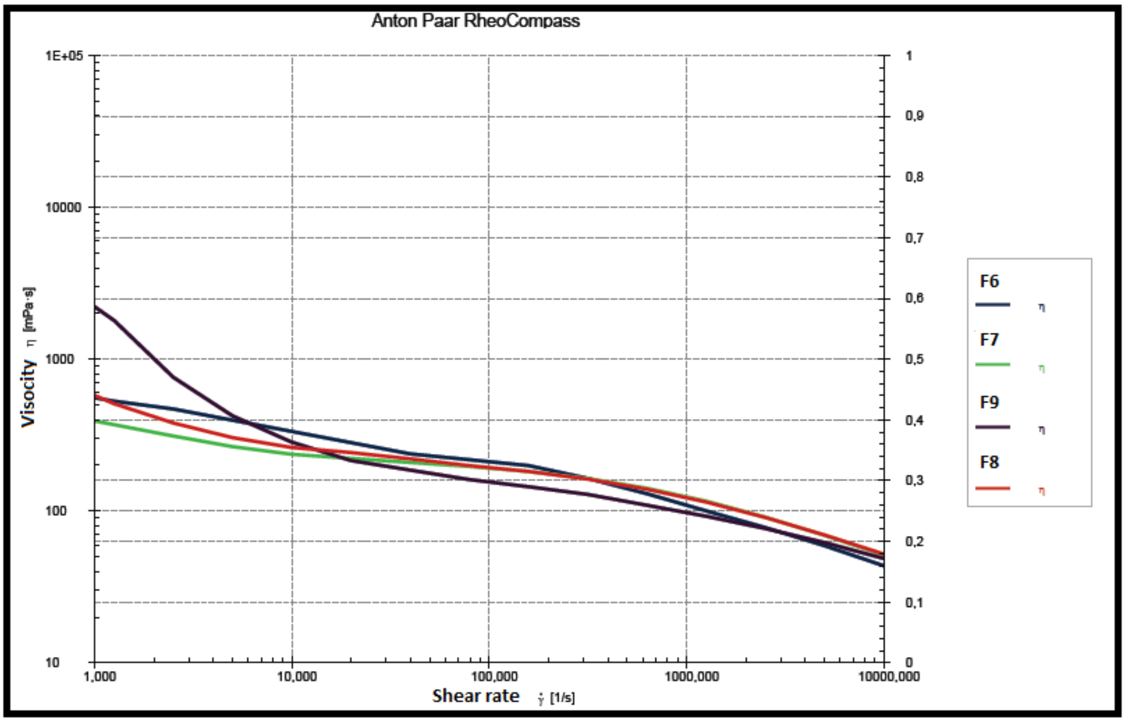


Figure 4.17- Flow curve for fillers F7-F9

4.6 First formulation

Table 4.20 summarizes the overall data attained with each resin in each phase of the process. Based on these informations, it can be concluded that reformulation of the anti-tannin primer should be based on R1, V1 or C1.

Table 4.20- Summary of the outcomes of the different phases (Characterization of resin, Effect of special anti-tannins additives and Effect of fillers).

Resin	Description			Result
	Pvc adhesion	Tackiness	Tannin	
R1	✓	✓	✗	✓
	Works only with using XXXX ,changes required to decrease Tackiness.			
R2	✗	✗	✗	✗
	No effect of anti-tannin additive.			
R3	✗	✗	✓	✗
	Only tannin are blocked using XXXX .			
R4	✗	✗	✗	✗
	No effect of anti-tannin additive.			
R5	✗	✓	✓	✗
	R5 resin cannot be used further due unavialiability from source. Besides having good results.			
R6	✗	✗	✗	✗
	No effect of anti-tannin additive.			
S1	✓	✗	✗	✗
	High drying time which cannnot be reduced.			
V1	✓	✓	✗	✓
	Works good without additive, changes required to increase in blocking tannins.			
O1	✓	✗	✗	✗
	No effect of anti-tannin additive.			
C1	✓	✗	✓	✓
	Works good without additive, changes required to decrease Tackiness.			
A1.1	✓	✗	✓	✗
	Change in formulation reduces the tannin property, besides it takes more time for drying.			
A1.2	✓	✗	✓	✗
	Tackiness cannot be improved due further changes in system.			

4.6.1 Strategies for reformulation

The changes in the formulation are exhibited in figure 4.18. C1 and R1 are provided with more matting agent to resolve the problem of tackiness. On other hand, a different technology is introduced using two coating i.e. V1.1 as a sealer and O1.1 as a topcoat. V1 is introduced with filler F9 and XXXX, also removing pigment.The sealer V1.1 must have less opacity, but the main objective is to block the tannin. O1 includes XXXX, but the objective is to give opacity and adhesion to PVC in the topcoat O1.1. Overall O1.1/V1.1 follow with the objectives shown in pictorial presentation figure 4.19.

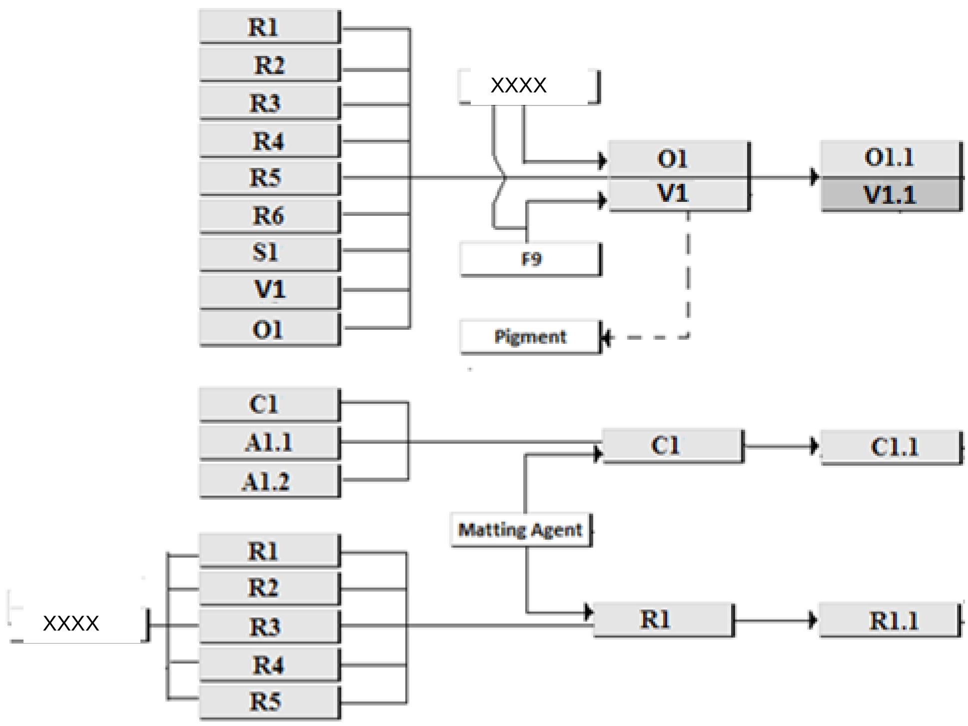


Figure 4.18- Scheme of reformulation for O1.1/V1.1, C1.1 and R1.1.

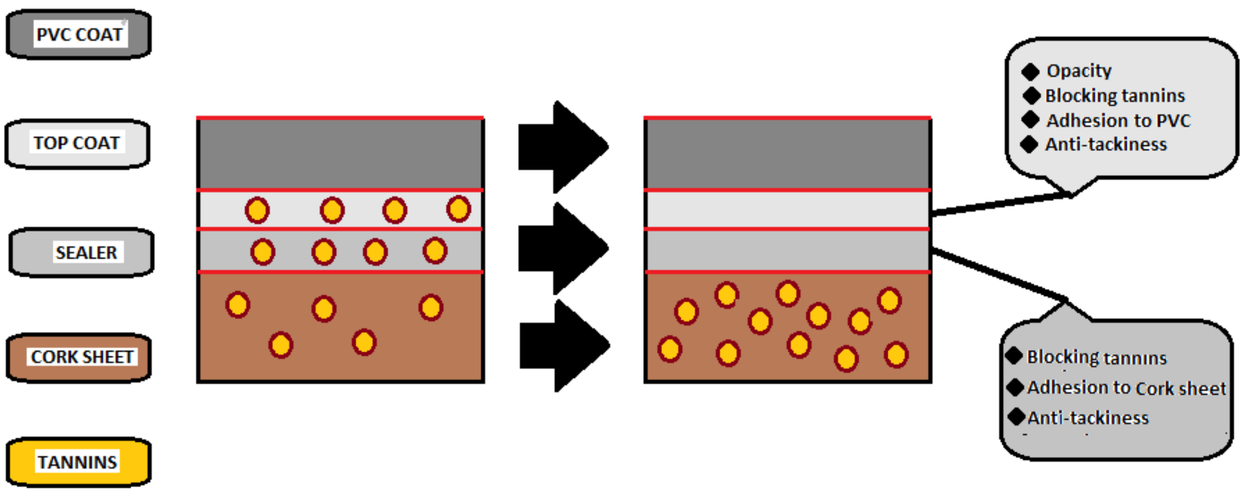


Figure 4.19- Pictorial presentation of O1.1/V1.1 with the set objectives.

After reformulation, several tests (Part 1- Viscosity, pH, Settling, Opacity, Gloss; Part 2- Adhesion to PVC, Test for tackiness, Adhesion to cork; Part 3- Tannin test; Part 4- Rheology test; Part 5- Climatic test) were performed, which results are then discussed.

4.6.2 Part 1- Viscosity, Settling, Opacity, Gloss

Table 4.21 shows good results in stability with maintained viscosity and no settling formed. pH ranges is maintained in each formulation except in O1.1. However, since O1.1 is a topcoat, pH is not concerned as far as opacity is good. V1.1 opacity is the lowest, which is of less priority than the pH. Concerning gloss values, these are adequate for C1.1 and V1.1.

Table 4.21- Results of Part 1- Viscosity, ph., Settling, Opacity, Gloss for Final scheme.

Resin	Viscosity Stability		pH	Settling	Opacity	Gloss		
	Viscosity (CF4)	Stable				20º	60º	85º
C1.1	33	Yes	5.0	No	85.8	1.4	2.3	7.4
R1.1	33	Yes	7.2	No	88.7	2.0	4.7	12.5
O1.1	20	Yes	8.3	No	88.2	1.4	5.1	11.2
V1.1	33	Yes	6.8	No	17.3	0.5	2.0	4.5

4.6.3 Part 2- Test for tackiness, Adhesion to PVC and cork

Further reformulation of R1.1 failed to reduce tackiness and adhesion to PVC (Table 4.22). C1.1 and O1.1 still had positive responses toward all tests. V1.1 failled the test for PVC but it was less tacky. Adhesion of cork is seen in all resins.

Table 4.22- Results of Part 2- Test for tackiness, Adhesion to PVC and cork for Final scheme.

Resin	Adhesion to PVC	Blocking	Adhesion to cork
C1.1	Pass	Pass	0
R1.1	Fail	Inconclusive	0
O1.1	Pass	Pass	0
V1.1	Fail	Pass	0

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4.6.4 Part 3- Tannin test

Reduction of blocking tannin property was detected in C1.1 and R1.1 (Table 4.23) which concludes failure for C1.1 and R1.1. Combining O1.1/V1.1, i.e. topcoat and sealer, results the same as V1.1 originating good anti-tannin coat overall (table 4.24).

Table 4.23- Results of Part 3- Tannin test for Final scheme.

Resin	Tannin test	Visual	Resin	Tannin test	Visual
C1.1	Inconclusive		O1.1	Fail	
R1.1	Inconclusive		V1.1	Pass	

Table 4.24- Results of Part 3- Tannin test for O1.1/V1.1.

Resin	Tannin test	Visual
O1.1/V1.1	Pass	

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4.6.5 Part 4- Rheology test

Flow curve

The flow curves for the final schemes of formulation are presented in Figure 4.20. C 1.1 carried on with same behavior with being slight downward Newtonian and higher viscosity at lower shear rates and lower viscosity at higher shear rates but above O1.1 which lowest among all and presented the best result of this test. Same behavior follows with R1.1 and V1.1 after being re-formulate showing a flow curve with higher viscosity at higher shear rates and lower viscosity at the lower strain rates.

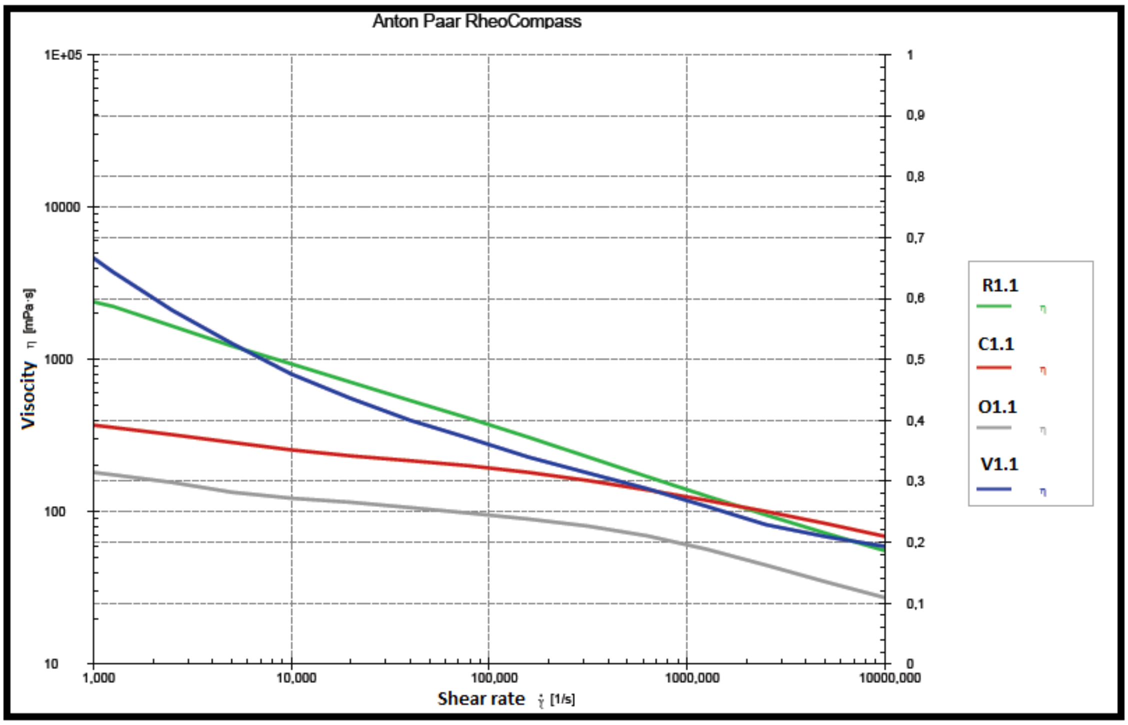

Figure 4.20- Flow curve for Final scheme

4.6.6 Part 5- Climatic chamber test

Results of the climatic test of resin C1.1 and R1.1 are shown in table 4.25. Clear differences after a span of time are observed in both. O1.1/V1.1 coat (table 4.26) shows no appearance of tannins in artificial aging with severe temperature and humidity. Stability of tannins in coat can be seen in different weather conditions.

Table 4.25- Results of Part 5- Climatic chamber test for C1.1 and R1.1.

Climatic test	C1.1	R1.1
Before		
After		
Result	Fail	Inconclusive

Table 4.26- Results of Part 5- chamber test for O1.1/V1.1.

Climatic test	O1.1/V1.1
Before	
After	
Result	Pass

5 Conclusions and suggestions for future work

In this project, a water-based paint to be applied directly to cork sheets was developed to block tannins migration and to adhere to PVC sheet while presenting less tackiness.

The results of the solubility tests of tannins in a co-solvent and in water at different pH proved the importance of-maintaining the lowest pH in the range 4-6. Based on these considerations, the chosen solvents were XXXX, XXXX, and XXXX. These tests also contributed to optimize the formulation with binders, anti-tannin agent and extenders.

Selection of the resin was the most crucial part of this project. The resins V1, C1 and R1 showed appropriate behavior regarding tannins blocking, gluing strength to a PVC sheet and tackiness. Based on the overall assessment of the results, the resin was reformulated by the inclusion of the optimum anti-tannins additives i.e. XXXX and the filler/extender F9 to achieve the final resin composition. Among the revised versions, V1.1 demostrated to have good tannins blocking performance and less tackiness but not enough gluing strength to a PVC sheet. Thus, to improve this last parameter, a new strategy was implemented, i.e., the use of two coatings: V1.1 as a sealer and O1.1 as a topcoat. The two coating system gave positive response to tannin blocking performance, gluing strength to a PVC sheet, less tackiness, climatic chamber test, QSUN and QUV.

5.1 Suggestions for future work:

Following are some suggestions of tests that aim optimization of the developed product:

1. A near neutral pH and a fast-drying time are important factors in preventing tannins staining of the topcoat. The research and development to create new binders with improved tannin blocking properties is very important. Most common binders in the market are more adapted to wood and not cork. Cork is a much worse material for tannin stains. New formulations with special binders for cork could provide even better results.
2. Cork is a very non-uniform material. Several applications are needed for one formulation to be sure that the anti-tannin result is valid. Results can be different depending on the cork agglomerate type, and even in the same cork sheet we can have an area with less tannins an another with more. A better way to test could be proposed.

3. Tests of others anti-tannin fillers that could bring great improvements in blocking tannins and reduce tackiness in the system.
4. To better test the reologic behavior of the paints other tests can be performed in the Reometer: frequency sweep test to study the long-term stability of paints to estimate and control the durability of optimum paint conditions; and the amplitude swepp test to study the storage modules by seeing any sedimentation of paints and its ease of application.

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