

RELEASE PAPER: CAN PHOSPHATE ESTERS BE AN ALTERNATIVE TO SILICONE?

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Release paper is a special paper grade with one or both sides coated with non-sticking materials. Silicone is currently the only material used to produce release paper at the industrial level. Its remarkable properties and availability ensure product quality and sustainability of the industrial production. Meanwhile, the stability of silicone polymers raises serious environmental problems in terms of paper substrate recyclability. Studies are currently under way to evaluate the ability of phosphate esters as a new class of compounds capable of developing non-adhesive surface properties. This paper presents initial attempts to coat the paper with phosphate esters and to assess phosphate ester / fibrous substrate and phosphate ester / adhesive interactions. The results show that this class of compounds exhibits non-adhesive properties and, when coated on paper under certain conditions, can lead to a non-sticking surface. Despite the fact that there is a long way to achieve ester anchoring to surface fibers and to control the peeling force from an adhesive tape, preliminary results are encouraging.

Keywords: Release; Paper; Phosphate ester; Silicone; Surface energy; Peel force

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BACKGROUND

Release Liner and Release Paper

Release liner is a substrate carrier web material that has one or both sides coated with a non-sticking material, which provides a release effect against any type of tacky material such as adhesives. The substrate can be paper or plastic-based, while the release agents employed have consisted almost exclusively of silicone material. Among the main uses of these products one can mention pressure sensitive adhesives (PSA) - label stock; tapes; medical and hygiene applications; graphic arts; industrial goods; building and insulation applications, etc. The worldwide production of release liner in 2010 was about 34 billion square meters (more than 2 million tons), with the PSA-label stock commanding more than 50% of the market share. Paper remains the main coating substrate with 85% of the global market share, compared to 15% for plastic films. The detailed situation of substrate types used in 2010 was presented by Spaulding et al. (2010): 41% glassine/calendered kraft papers, 17% polyolefin coated papers, 15% clay coated papers, 15% plastic films, and 12% other papers.

The release paper is in fact a release liner whose backing is made of paper. Since paper dominates the market today, we will refer to it hereafter. The main functions of the

release paper, as it is suggested in Fig. 1, are to protect the adhesive during transit and storage and, ultimately, easily release the PSA label for its intended use.

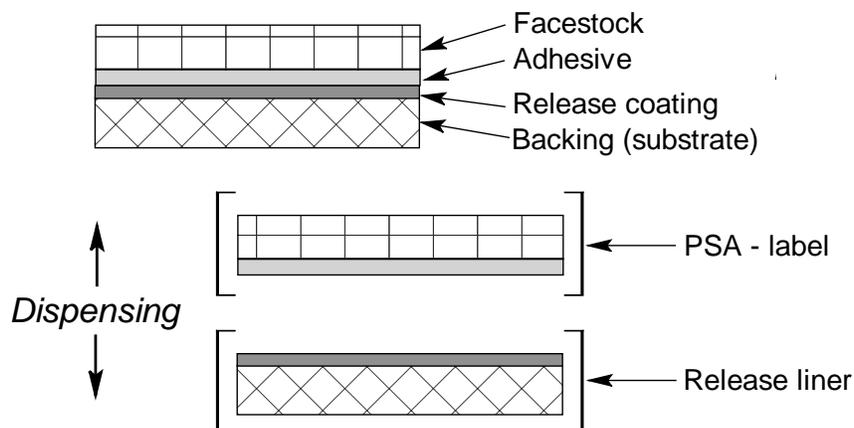


Fig. 1. Structure of a self-adhesive label laminate

Silicone Release Agent: Chemistry and Properties

Nowadays, silicone-based materials are the universal release agent used to produce release paper. The term “silicone” refers to a general category of synthetic polymers with a siloxane main chain made of repeating silicon to oxygen bonds. In addition, each silicon atom is bonded to organic groups, typically two methyl groups, in which case the material is called polydimethylsiloxane (PDMS) (see Fig. 2). The simultaneous presence of organic groups attached to an inorganic backbone gives silicones a combination of unique properties such as high thermal and chemical stability (due to the siloxane main chain) associated with strong hydrophobic behavior and low surface free energy (due to methyl groups), making them ideal release agents (Bondurant et al. 1999; Colas and Curtis 2004; Colas and Cray 2007). Besides, silicone polymers are liquid under normal conditions up to quite high polymerization degrees and show high wettability to almost all solid surfaces, a characteristic that facilitates the subsequent coating process.

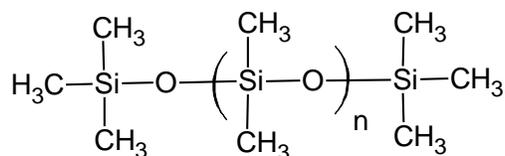


Fig. 2. Chemical structure of polydimethylsiloxane (PDMS)

Once coated on the paper substrate, the liquid silicone film must undergo a crosslinking reaction, referred to as “silicone cure chemistry”, which changes the silicone’s state of matter from liquid to solid. This process aims to create a network of chemical bonds among silicone polymer chains (to limit the amount of free silicone migration to adhesive), and between silicone and functional groups present at the paper surface (to anchor the silicone film to the paper substrate). Usually, the silicone cure

chemistry involves the use of catalysts, activation energies, and the existence of a small number of reactive functional groups (e.g. silane, vinyl, hydroxyl, epoxy, and acrylic) on the PDMS macromolecules in place of the inert methyl groups (Colas and Cray 2007). The silicone crosslinking by addition, whose global reaction is presented in Fig. 3, accounts for more than 80% of currently available silicone cure mechanisms (Holwell 2008).

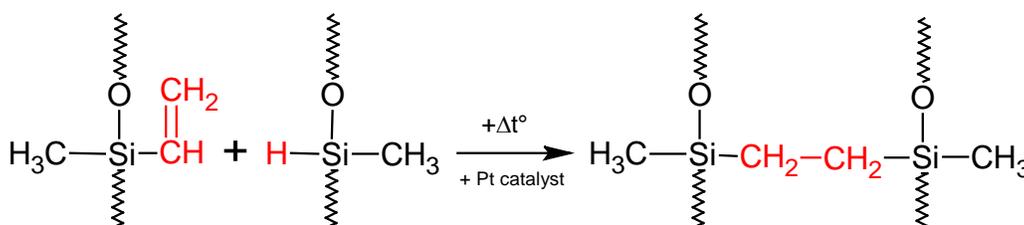


Fig. 3. Silicone thermal addition cure chemistry

Cured silicone films generally have a thickness of 1 to 2 μm , a basis weight of 1 to 2 g/m^2 , and exhibit anti-tack properties against a wide range of adhesive formulations. The main drawback of using silicone as release agent is that it makes difficult the further recycling of paper substrate, thus losing a significant amount of high quality fibers.

Phosphate Esters as Release Agent

It is well known that phosphoric esters of organic hydroxyl compounds are amphiphilic molecules with a polar phosphate head and one to three non-polar alkyl tails. Their stability and surfactant nature make them appropriate for use as cleansing, emulsifying, and antistatic agents, rust inhibitors, etc. In particular, salts of phosphate monoesters are useful for articles that are used for direct contact with human bodies, such as shampoo and cleansing agents, because they have good water solubility, foaming properties, and cleansing power, exhibiting low toxicity and low skin irritability (Tsuyutani et al. 2004; Kurosaki and Akio 1982). A review of patents published during the last 30 years shows that many claims have been made about the efficiency of phosphate esters in several pulp and paper applications such as ink collection in flotation deinking (Van den Haak 1981), production of grease-resistant paper when added to the pulp suspension with a fluoropolymer (Sansho Co. 1982), felt conditioning (Khan and Owiti 1992), gloss improvement of calendered paper (Woodward 1980), etc. However, there is very little literature explaining the effect of phosphate esters on pulp or paper properties.

In previous studies we have tested the ability of specific phosphate esters to reduce the linting propensity of offset paper (Brouillette et al. 2006). It was found that adding certain phosphate esters to the pulp suspension prior to web formation could reduce paper linting and dusting by 40% (Brouillette 2010). Phosphate esters retained in the sheet decrease the surface free energy and act as “internal” release agent, preventing fiber lifting during sheet drying and printing without affecting the optical and strength properties of the sheet. A later study demonstrated the formation of covalent bonds between cellulose and phosphate hydroxyl groups during paper drying (Ly and Brouillette 2010).

Given the surfactant properties of phosphate esters and their interaction with pulp fibers, we have proposed to take advantage of the “internal” release properties of phosphate esters by coating them on a paper surface. Starting from the problem of silicone release paper recycling, our main research objective was to evaluate the ability of phosphate esters as a new class of compounds capable of developing release properties, allowing the subsequent recycling of paper substrate. This paper presents initial attempts to coat the paper with phosphate esters and to assess phosphate ester / fibrous substrate and phosphate ester / adhesive interactions.

EXPERIMENTAL

Materials

Phosphate esters (PE): Synthesis, analysis and purification

Two phosphate esters were synthesized by the reaction of phosphoric anhydride with two linear fatty alcohols: 1-octanol (C8) and 1-octadecanol (C18). For the reaction shown in Fig. 4, the mole ratio of reactants (fatty alcohol, P₂O₅ and H₂O) was 2:1:1. The reaction conditions were chosen in order to promote the formation of phosphate monoester (Tsuyutani et al. 2004; Kurosaki et al. 1982). Also, the ratio of mono- and diester is closely related to the alkyl chain length of alcohols, increasing with the chain length (Hadj Bouazza and Brouillette 2010). Quantitative analysis performed after the esterification reaction gave the following proportions: 80% mono- and 20% diester for the C8 alkyl chain and 100% mono- and 0% diester for the C18 alkyl chain.

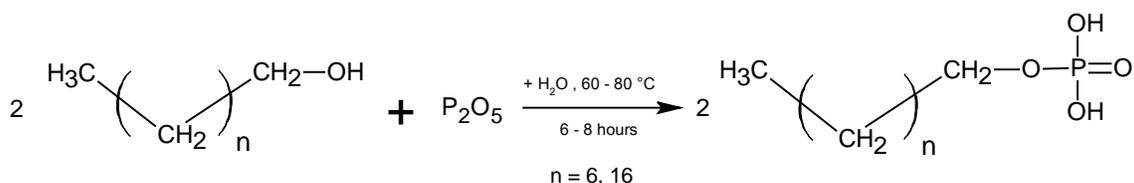


Fig. 4. Phosphate esters synthesis reaction

Inevitably, the final product will consist of a mixture of phosphate esters, unreacted fatty alcohol, phosphoric acid, and other by-products. In order to isolate the desired product, a purification and analysis plan was developed, consisting of three successive water/solvent extractions. The purified product is a white solid compound at room temperature, composed predominantly of phosphate monoester (~100% for C18 and 90% for C8). The melting point of the product depended on alkyl chain length: 60 to 70°C for C18 and 20 to 30°C for C8.

Low porosity paper

All coating tests were carried out on a special paper substrate made on a pilot paper machine located at the Centre Spécialisé en Pâtes et Papiers (CSPP) in Trois-Rivières, Canada. This unsized calendered paper has about 85 g/m² basis weight and is made of highly beaten softwood kraft fibers as the main fibrous furnish component. The papermaking conditions lead to a low porosity paper, as low as 5 mL/min PPS porosity.

Polyvinyl alcohol (PVA)

The PVA used was 99% hydrolyzed with a molecular weight distribution ranging from 85,000 to 124,000. It was solubilized in water at 10% concentration. The addition of PVA to the sheet had two main purposes: (1) as a coating material, creating a physical barrier at the paper surface in order to prevent the penetration of the phosphate ester into the paper structure; and (2) in a mixture with the phosphate ester to control the release force vs. adhesive and anchoring force vs. paper substrate.

Methods

Paper coating

The laboratory coating device was composed of a flat worktable on which the substrate to be coated was placed. The active element of the coating device is a Mayer rod that is inserted in two interconnected pockets driven by a motor simultaneously describing a translation movement parallel to the table. The paper sheet is fixed on the table, and the coating sauce is deposited on the sheet at the end where the rod is placed. The sauce is distributed evenly on the surface when the bar is driven into motion. The amount of material deposited depends on: the size and number of Mayer rods, the relative distance between the rod and surface to be coated, and the coating color. Meanwhile, rod speed or the mixture's viscosity will significantly influence parameters related to the quality of the coating such as the formulation's surface distribution or structure penetration ability. Frequently the coating step is followed by a thermal treatment aimed at evaporating the water from the coating color and/or consolidating the coated layer. In our case, the coating delivery system was: 10% PVA solution, 5% C18 phosphate ester dispersion, and 100% solids for the C8 phosphate ester (the compound is liquid at room temperature). An excess of ester was applied on the paper to ensure that surface properties are due mainly to the coated layer and not to the paper surface. The estimated thickness of the phosphate ester layer is about 10 μm , as calculated from the density and the basis weight of the coated sheet.

Surface free energy (SFE) measurement

SFE characterizes the thermodynamics of solid surfaces and is the first and most important parameter that allows the evaluation of the adhesion properties of materials. Usually, the anti-tacking properties are associated to low surface free energy materials having a major dispersive energy component.

Different approaches are used to determine the energy of solid surfaces, contact angle measurements being the most common. Starting from Young's equation, several variants of this method have been developed. An idea presented by van Oss, Chaudhury, and Good is the SFE partition into two independent components: dispersive and polar. The authors also divided the polar component into two other subsequent components: acid and base, and proposed an equation with three unknowns that links all these partitions (Żenkiewicz 2007). Measuring the contact angles of three well known liquids on the same solid surface, a system of three independent linear equations is generated. The mathematical solutions of this system are in fact the SFE and its components.

Five contact angle measurements for each liquid were made with a FTA4000 Microdrop® device manufactured by First Ten Ångströms. The device allows deposition

on solid surfaces of very small droplets (as low as picoliter volume) and can capture up to 300 images in less than 5 seconds. All droplet geometry data, including the contact angle, are then determined for each image with the FTA32 Video software. Ethylene glycol, formamide and water (as bipolar), and α -bromonaphthalene (as nonpolar), were used as reference liquids for SFE measurements.

Peel force measurement

The peel test measures the strength required to pull apart bonded surfaces composed of a standard adhesive tape and a coated paper sample. This method was adapted from ASTM F88-99 (ASTM 1999) and is made at a 180° supported separation angle, under controlled conditions: 23°C, 50% relative humidity, 50 mm/min peel rate (100 mm/min relative to the top grip), 25.4 x 75 mm (width × length) size sample. The double-coated adhesive tape is attached on one side to a rigid alignment plate and on the other side to a paper sample. One couch roll (13 kg weight), is rolled backward and forward 10 times with no supplementary pressure being applied to promote the adhesion between surfaces. This assembly is mounted into an INSTRON device model 4201 with the rigid plate tail held in one grip and the sample tail, folded at 180°, and held in the opposing grip while the test is being conducted. At the end of the test, the Bluehill software is used to calculate two important parameters: the peel force, as the average of the highest 5 load peaks, and the absorption energy, as the integrated area at average load. Two peel tests were conducted for each sample, the results being expressed as the arithmetic mean of the two measurements. Besides these measurements, each test is accompanied by a visual evaluation of the peeled surfaces to identify the mode of specimen failure.

Surface topography analysis

Optical profilometry is a rapid, non-destructive, and no-contact surface metrology technique. An optical profiler is a type of microscope whose working principle is based on “white light interferometry”. In its most common application, interferometry is a versatile measurement technology for 3D imaging of surface topography with very high precision. In this study, an optical profiler WYKO NT1100 (Veeco) was used to observe the changes in paper surface micro-geometry as a result of the coating process. The paper roughness (Ra) is the second parameter which can be measured by the profilometer and usually comes as a further statistical interpretation of surface images. The roughness results shown in Fig. 7 are the arithmetic mean of Ra for the five surface images captured for each sample.

Paper barrier properties

Barrier properties of the low porosity paper substrate, coated or uncoated with phosphate esters, thermally treated or untreated, were tested according to TAPPI methods:

- Air permeability by PPS (Parker Print Surf) Porosity method (TAPPI T 555 om-99),
- Water permeability by Cobb method (TAPPI T 441 om-98),
- Grease permeability by Castor Oil method (TAPPI T 559 cm-02).

RESULTS AND DISCUSSION

Barrier Properties and Surface Free Energy

Theoretically, the main idea is to coat the paper with mono-phosphate esters and induce a thermal reaction between the two remaining free hydroxyl groups of phosphate function with the corresponding hydroxyl groups of cellulose fibers. In this way, we can make sure that the ester anchors to the paper surface, “hiding” the polar phosphate side and exposing the nonpolar alkyl chain side to a future adhesive formulation. The initial coating attempts were made with the C18 phosphate ester. The coated paper exhibited excellent barrier properties (almost a water and greaseproof paper, see Table 1) and low surface free energy, as we can see in Table 2, because of the large size of the alkyl chain. However, the ester proved to be an inert product at the paper surface, easily migrating to the adhesive tape during the peel test.

Table 1. Barrier Properties of the Papers Coated with Phosphate Esters

Paper	Characteristics / Standard Deviation			
	Coat basis weight (g/m ²)	Porosity PPS (ml/min)	Water permeability (g/m ²)	Grease permeability
Uncoated	0 / 0	7.5 / 0.3	116 / 10.8	0 / 0
PE (C8) coated	10.9 / 0.3	0 / 0	47 / 2	11.6 / 0.5
PE (C18) coated	11.6 / 1.1	0.4 / 0.1	16 / 1.3	11.8 / 0.4

These results led us to synthesize a second phosphate ester with a much shorter alkyl chain consisting of eight carbon atoms (C8). Although the barrier properties of this were found not to be as good as those of C18, and the product was characterized by a high SFE value that can impair the anti-tacking properties, it had at the same time important polar and base SFE components, like PVA and paper, which enhance their reaction compatibility (see Table 2).

Table 2. SFE of Different Materials Measured by the Van Oss-Chaudhury-Good Method

Material	SFE (MJ/m ²) / Standard deviation				
	Total	Dispersive	Polar	Acid	Base
Silicone	25.98 / 0.74	25.98	0	0	0
Phosphate ester (C18)	17.70 / 0.68	16.66	1.046	0.4752	0.5755
Phosphate ester (C8)	38.35 / 2.08	33.73	4.625	0.4061	13.17
Polyvinyl alcohol	39.89 / 1.75	27.15	12.74	1.330	30.49
Low porosity paper	46.27 / 2.46	41.76	4.507	0.1434	35.42

Release Properties

The PE (C8), which was in a liquid state at room temperature and during coating, successfully penetrated even a closed structure like the low porosity paper. Consequently, the coating became rather a paper impregnation process. Despite this, it was interesting to see the sample responses to repeated peel tests, given that they were thermally treated for 6 hours at different temperatures (Fig. 5). All coated papers with PE (C8) easily peeled off from the adhesive tape. The release force increased with the number of peel tests. This clearly shows the anti-tacking properties of PE (C8) but also its migratory behavior

with repeating of the peel test. The results from Fig. 5 show that thermal treatments bring insignificant changes to the peel force. We can conclude that even at high temperature, there are only limited interactions between the C8 PE and cellulose fibers.

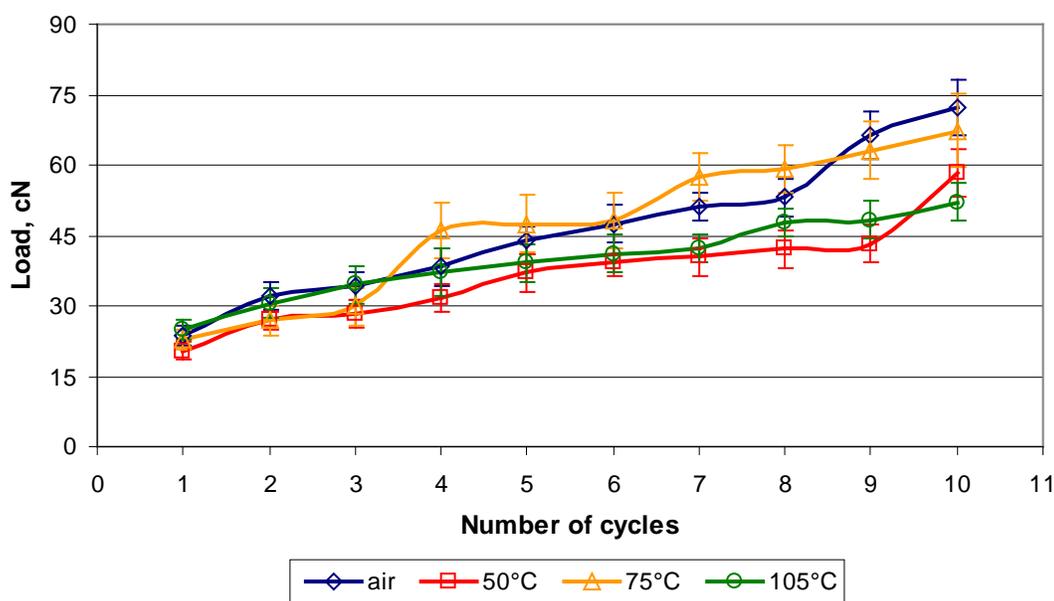


Fig. 5. Influence of thermal treatments and number of peel test cycles on the peel force value

Two solutions were proposed to limit the C8 PE penetration into the paper structure. The first attempt was to apply a PVA barrier layer at the paper surface before the PE coating (PVA/EP), and the second was to use a viscous mixture of PVA and PE as coating formulation (PVA+PE). The peel test results of these samples are presented in Table 3. As expected, the adhesive tape caused the sample to break (tearing) in the cases of uncoated paper and PVA coated paper. The paper coated with 30% PVA and 70% PE mixtures showed release properties for the first peel cycle, but the coated layer was removed and the paper structure delaminated starting with the second peel cycle. Small fiber picking appeared on the PE coated paper surface after a sufficient number of peel cycles. The PVA/PE double layer coated paper was the only sample that was easily peeled off. The release force remained fairly constant, and the surface remained intact after more than 20 peel test cycles. These characteristics are the closest to those of the reference silicone-coated release paper.

Table 3. Peel Test Behavior of Coated Paper Samples

Coating composition	Coat basis weight (g/m ²)	Average peel force / St. dev. (cN)	Absorption energy (mJ)	Number of peel cycles	Note
PVA	2	3095 / 163	1512	1	Sample rupture
PVA + PE (C8)	4-8	360 / 32	140	2	Sample delamination
PE (C8)	10-12	72 / 3	31	>10	Small picking
PVA / PE (C8)	2/--	66 / 4	15	>20	Intact surface
Silicone	1	190 / 9	97	1	Intact surface

Surface Topography

The topographic images shown in Fig. 6 and the corresponding roughness values of Fig. 7 confirm in fact the results reported for peel tests.

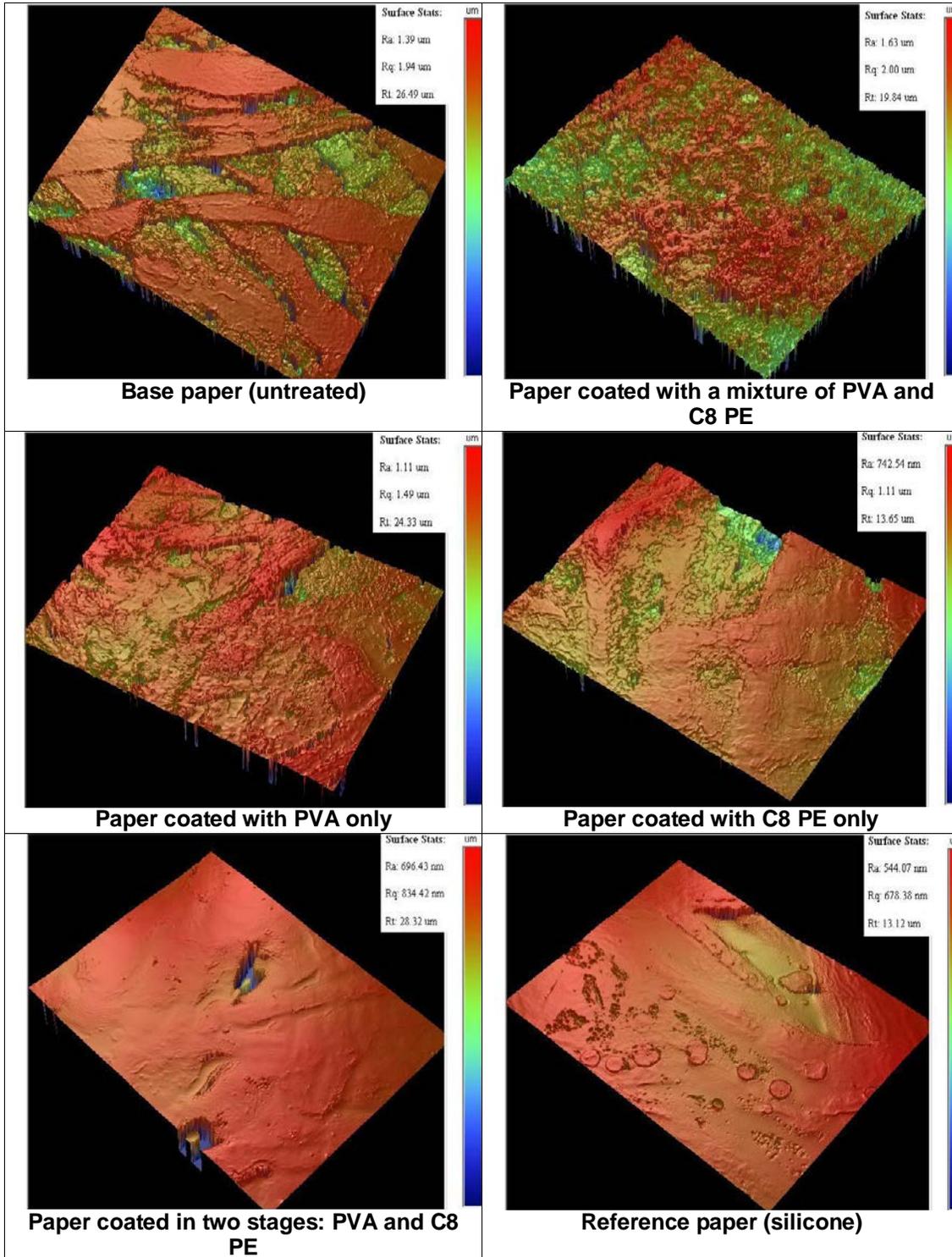


Fig. 6. Surface topography of paper treated with different coating formulations

Rough surfaces with high density of asperities, like uncoated paper or PVA and PVA+PE coated papers, promoted adhesion by a mechanical interlock mechanism, while the hydroxyl polar groups of these materials led to an adsorption adhesion mechanism as a result of secondary intermolecular forces at the interface. By contrast, the adhesive bonding was quite limited for PE- and PVA/PE-coated papers due to much smoother surfaces and nonpolar alkyl chain exposure at the interface. The surface topography and roughness value of PVA/PE and silicone coated papers looked very similar, but these papers were quite different in terms of peel force. The silicone release paper provided some residual adhesion that kept the adhesive “bonded”, while the PVA/PE coated paper had almost “no bonds” to it.

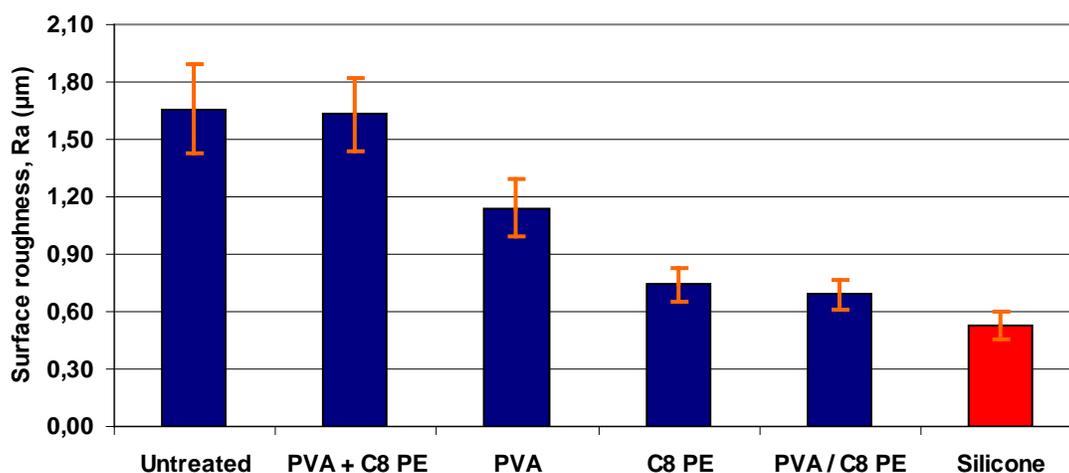


Fig. 7. Changes in paper surface roughness as result of the coating process

CONCLUSIONS

The phosphate esters of fatty alcohols are compounds that exhibit anti-tacking properties, as proven by peel tests and surface free energy measurements. The interaction of the phosphate ester layer with the paper surface is quite limited, leading often to a mass transfer when the adhesive tape is peeled off. However, it seems that anchoring occurs when esters and coating surfaces present similarities in term of SFE (like total energy level and/or energy component distribution). Despite the fact that it is not yet possible to control the anchor and release processes as with silicone polymers, these first results are encouraging.

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