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PHYSICAL AND CHEMICAL PROPERTIES OF CONVENTIONAL PATTERN WAX AND REFORMULATED PATTERN WAX USED IN INVESTMENT METAL CASTING.

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ABSTRACT

The present study reports experimental results obtained for the physical and chemical properties of conventional or standard pattern wax and reformulated pattern wax blended in order to obtain maximum efficiency for possible recycling in the investment metal casting industry. Some of the properties determined included melting point, flash point, water content, ash content, volumetric expansion, hardness, refractive index, infrared and ultraviolet spectra, thermal behavior, curves obtained by DSC, DTA and TGA. The reformulated wax was shown to be relatively stable and good for industrial use after twelve simulated recycling steps.

RESUMO

O presente trabalho apresenta resultados experimentais obtidos para cera padrão para modelos, convencionalmente utilizada pela indústria, e cera reformulada visando sua reciclabilidade quando utilizada no processo de microfusão. Algumas das propriedades determinadas foram: temperaturas de fusão e de volatilização, teores de água (voláteis), cinzas, dureza, módulo de elasticidade, Índice de refração, expansão volumétrica, espéctros característicos no infravermelho e ultravioleta e as curvas térmicas: DSC, DTA, TGA ou DTG. Os resultados obtidos mostram que a cera reformulada permanece relativamente estável depois de doze ciclos simulados de utilização e que ela é satisfatória para processos industriais de microfusão.

KEY WORDS: Pattern Wax, Metal Casting, Dewaxing, Recycling of Pattern Wax.

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INTRODUCTION

Pure beewax or common waxes modified with fats and resins have been used since ancient times in Europe, Asia end Africa, to make models that were invested with clays to give ceramic moulds from which metal casting especially bronze, were made. Art objects of high quality were manufactured in Italy during the 16^{th} century, but the lost-wax process only became of industrial importance with the development of dental metallurgy and particularly the advent of the turbine engine in the years preceeding World War II.[1-4]

The investment casting process is characterized by the manufacturing of parts of high metallurgic quality, especially with respect to complexity of design, dimensional aspects and surface finshing. In addition, investment casting is able to achieve the tolerance necessary to eliminate difficult or impossible machining operations. [4-10]

Waxes used for patterns are complex mixtures composed of selected, high-priced ingredients that have been formulated and blended by a wax supplier in order to make the best wax patterns possible.

Pattern wax is a very valuable raw material and represents the starting point for the production of investment casting. Obviously, the better the quality of the wax patterns prepared, the higher will be the quality of investment castings produced.

Waxes are generally classified into three cathegories: natural waxes, modified natural waxes and fully synthetic waxes. [11,12.] Natural waxes, widely distributed in nature, are usually classified into fossil and nonfossil or recent waxes. Among the more common fossil waxes are petroleum waxes that consist of long chain hydrocarbons and *monton* waxes that contain oxygen functional groups in the molecules. [12,13] Nonfossil or recent waxes include animal and plant waxes. By far, the most widely known is beewax produced by Apis mellifera and other bees of the Apis especies, but there are other insect waxes used on a large scale produced by bugs at the Coccidae family, the Chinese insect wax, being the most widely commecialized. Animal waxes come from land animals (e.g, wool wax) and marine animals (e.g. sperm whale or spermaceti wax). Among plant waxes the more common ones are carnaúba, an exudate of the carnaúba palm leaves produced commercially in Northern Brazil in the states Of Ceará and Piauí and candelilla wax obtained from a desert shrub, produced on a large scale in Mexico, in the states of Sonora and Chihuahua.[13]

Modified natural waxes are obtained from crude oil by physical refining methods or chemical processes involving paraffin or monton waxes [14].

Fully synthetic waxes may be hydrocarbon waxes or nonhydrocarbon waxes including amides, ethers alcohols, acids, polyethylene and Fischer – Tropsch waxes[15]. .

A wide majority of the pattern waxes available commercially are usually a blend of waxes, resins and additives selected to impart the necessary characteristics [16]. Among the desired features are strength, hardness, melting point, viscosity, surface smootheness, ash content, dimensional stability, shrinkage, toughness, mold release, injection temperature and compatibility with mold materials.

The purpose of the present study was to analyze physical and chemical properties of a typical pattern wax used by the regional investment casting industries in the State of Rio Grande do Sul, Brazil and evaluate the possibility of recyclinig, making the necessary adjustment in the formulation of the pattern wax blend.

Some of the properties determined included melting point, flash point, water content, ash content, volumetric expansion, hardness, refractive index, elastic modulus, viscous modulus, viscosity, complex viscosity, infrared and ultraviolet spectra and thermal behavior curves obtained by a differential scanning calorimetry (DSC) and a differential thermal analysis (TGA).

MATERIAL AND METHODS

The two model pattern waxes used in this study were prepared from commercial products. One model, the conventional or standard pattern wax, used by the regional investment casting industries in the State of Rio Grande do Sul, Brazil, consists of 48% by weight pitch, 20% mineral wax, 5% carnaúba palm wax and 2% ethylene vinyl acetate (EVA). The second model, a reformulated pattern wax, consisted of 38% pitch, 40% paraffin, 27% synthetic wax, 2% ethylene vinyl acetate (EVA) and 1% butylated hydroxytoluene (BHT)

The model waxes were prepared in a container equipped with heating and paddle stirring and a hot filtering system. The fusion processes were a performed as follows: a) melting of paraffin and mineral wax (120°c). b) addition and melting of EVA and pitch under continuous stirring until the temperature reached 90°c. c) addition and fusion of carnaúba palm wax. d) stirring for 30 minutes and e) warm filtration followed by cooling.

The microfusion process was simulated starting with 15 kg of pattern wax, dewaxing in an autoclave under the same conditions used by the investment casting industries 7,4 to 7,6 kg/cm^2 of pressure, 170 to 175 °C; 10 minutes dewaxing time followed by cooling and testing under environmental conditions for 24 hours. The reformulated pattern wax was subject to twelve (12) recycling processes.

The infrared spectra were obtained using KBr pellets with a Perkin-Elmer FT-IR Spectrum 1000 Spectrophotometer and the ultraviolet spectra were determined in cyclohexane solution containing 3mg/L of solute using a Shimadzu Model 160 /PC UV-VIS Spectrophotometer.

Thermal and termogravimetric analyses were performed using a TA instrument Model DSC-2010, with inert atmosphere, closed capsule and a heating rate of 10 °C/min and a Netzch Instrument Model STA-409 with an open capsule, an oxidizing atmosphere (a flow of 150 ml of air per minute) and a heating rate of 2,5 °C/min.

The water content of the wax was determined employing a Sartorius Model MA 30 Eletronic Humidity Analyzer at 105 ^{0}C for 5 minutes keeping the sample in equilibrium with a hygroscopic environment (60% humidity and –24 °C).

The characterization and monitoring during the successive cycles was done measuring the refractive index (Abbé refractometer at 80 °C with a precision of ± 0,0015); Young Elasticity Modulus (EMIC DL500 Apparatus at 24°C, 85% deformation of 10mm and a rate of 20 mm/min); Shore D Hardness; volumetric expansion (IBER-P-092 Technical Norm) and melting and Flash points using Differential Scanning Calorimetry DSC.

RESULTS AND DISCUSSION

Figure 1 shows the physical appearance of conventional pattern wax- (a) and (c) and reformulated pattern wax (b) and (d).

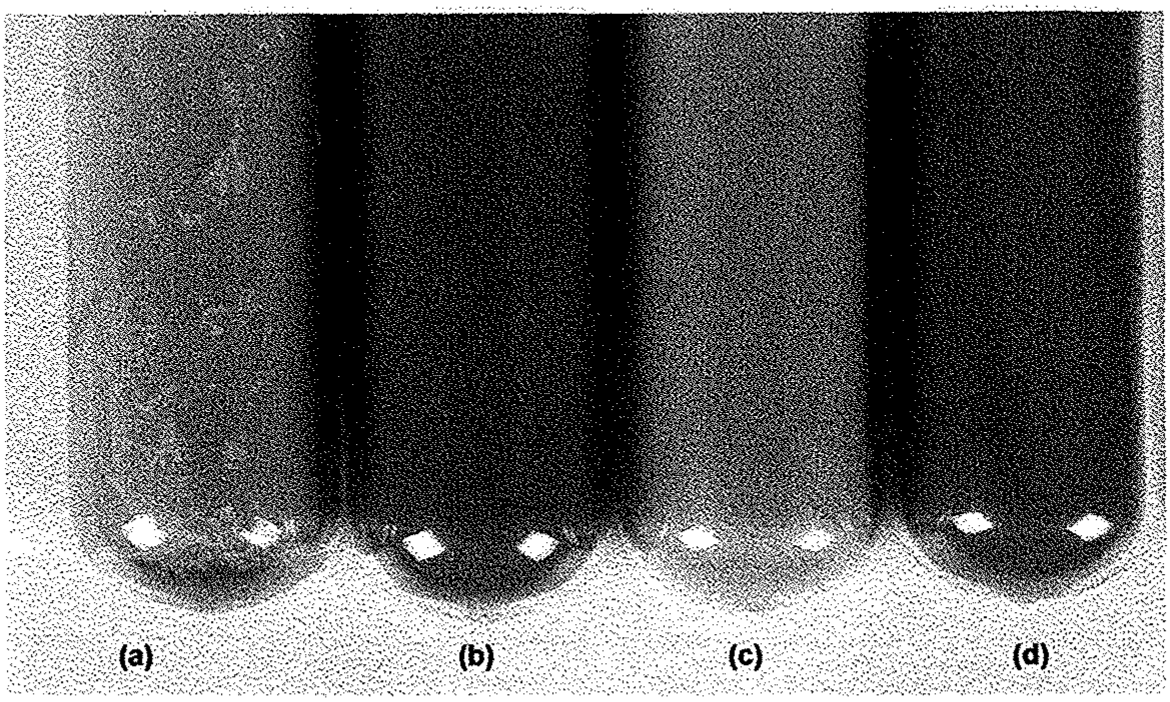

Figure 1. Physical Aspect of Conventional Pattern Wax a) Fused at Rest and c) Fused with stirring and Reformulated pattern Wax b) Fused at Rest and d)Melted with Stirring

The reformulated pattern wax shows no phase separations indicating that the desired structural stability has been achieved.

Figure 2 illustrates the infrared spectra of the standard or conventional pattern wax and the reformulated pattern wax. Absorption bands at 2907, 1469 and 717 cm^{-1} are characteristic ox waxes containing hydrocarbons (paraffins and mineral waxes). The bands at 2907, 1694 and 1277cm^{-1} are typical of acid waxes and the peaks at 3426, 1694 and 1181 cm^{-1} indicative of waxes that contain esters. It is worthwhile to note that no absorption bands occur about 1500 cm^{-1}, indicating the absence of saponificated carboxyl groups.

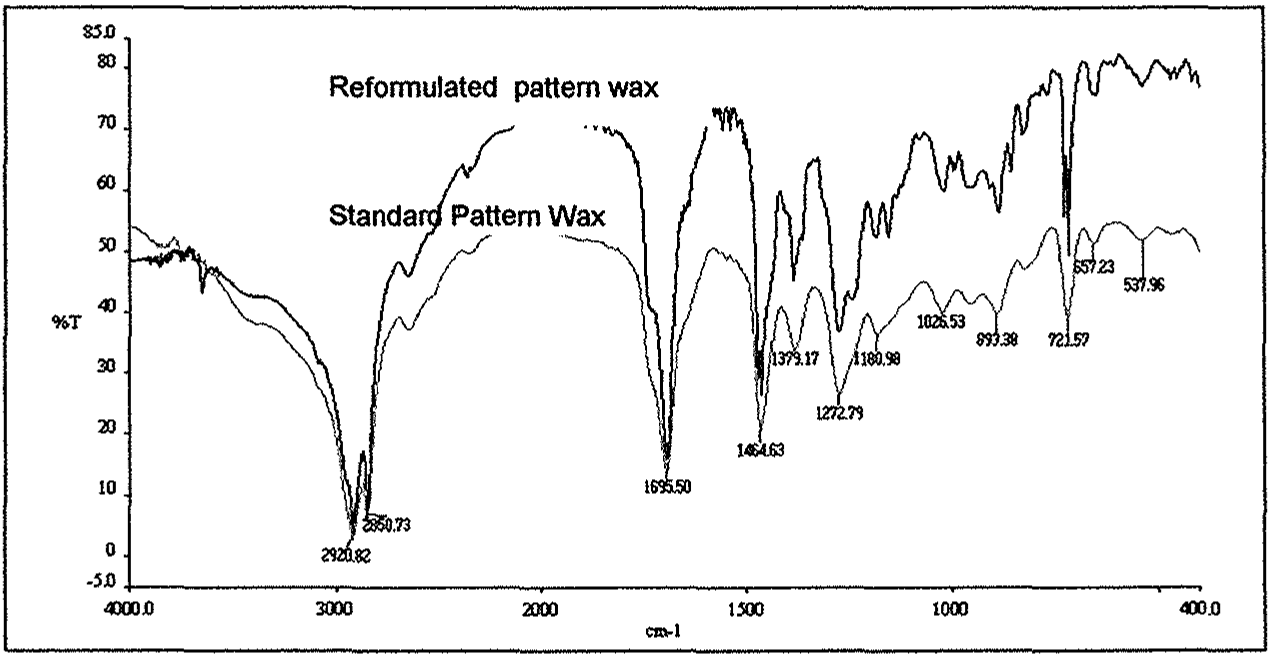

Figure 2. Infrared Spectrum of Standard of Conventional Pattern Wax and Reformulated Pattern Wax.

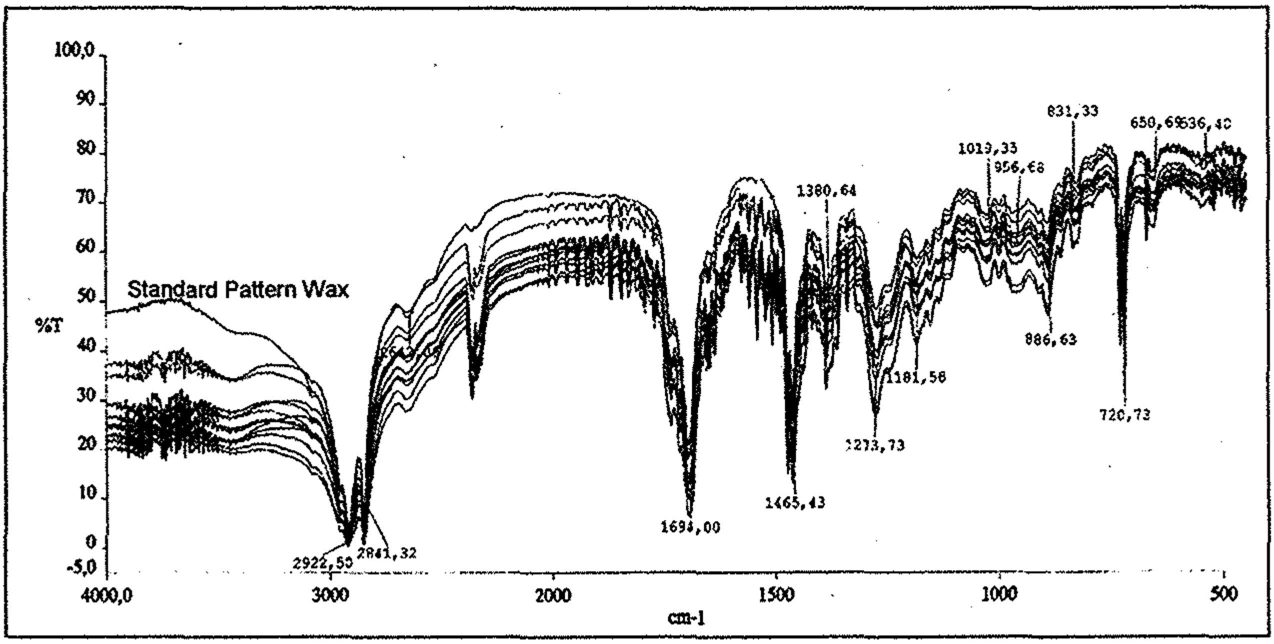

Figure 3. Infrared Spectrum of Reformulated Pattern Wax followed by Spectrum of Simulated Recycled Samples (Odd Numbers).

As can be seen in Figure 3 the recycling of the reformulated pattern wax (cycles 1,3,5,7,9 and 11) has little effect on the IR Spectrum as a whole, indicating the relative stability of the reformulated wax. It should be noted that the spectra were obtained after drying and filtering the recycled sample and removing the dark paticles from the dewaxed waxes.

Figure 4. shows the ultraviolet absorption spectra obtained for the conventional or standard wax and even – numbered recycled samples of reformulated wax.

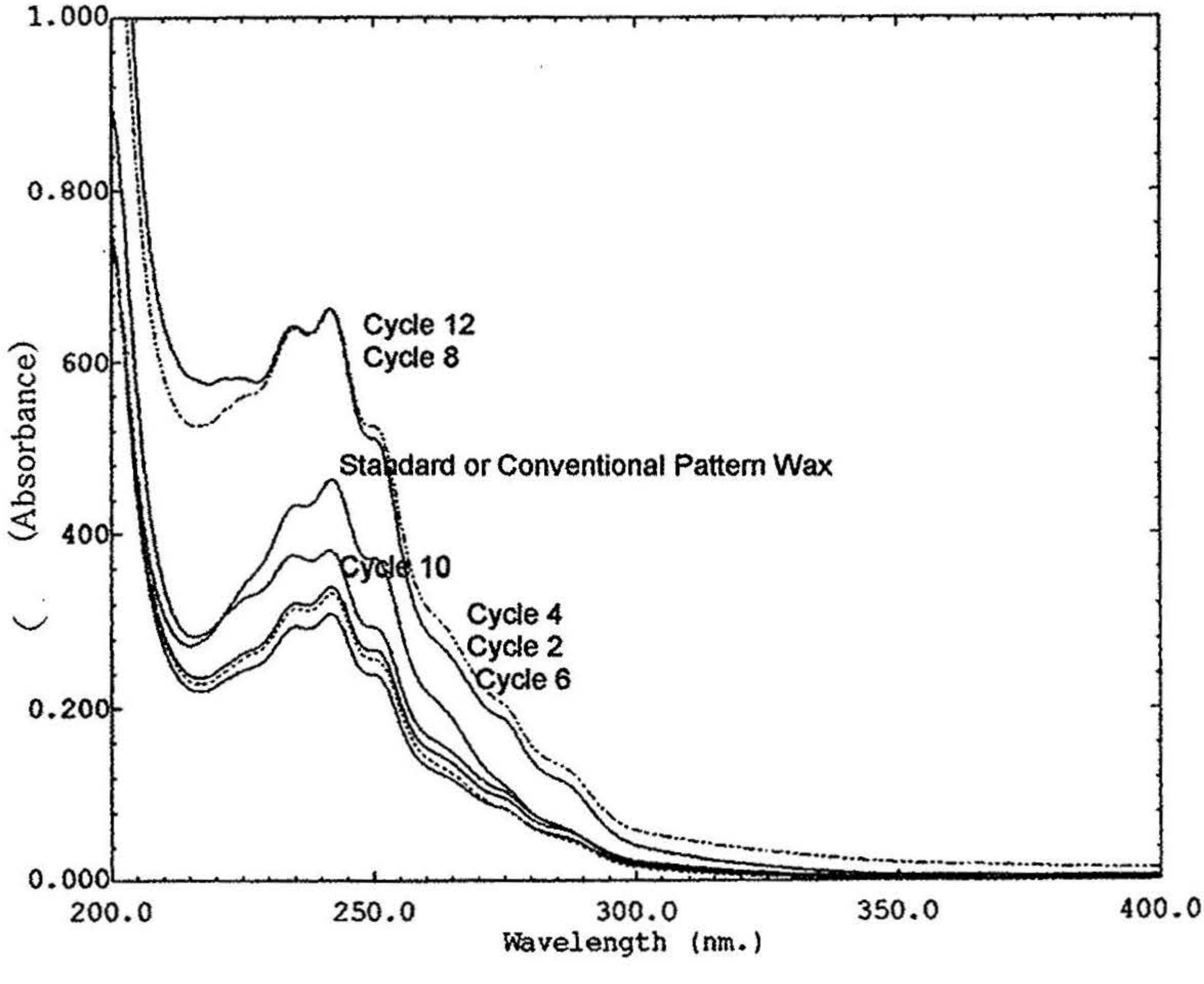

Figure 4. Ultraviolet Absorpition Spectra of Standard or Conventional Pattern Wax and Recycled Sample of Reformulated Pattern Wax (Even – Numbered Cycles).

Some changes in the spectra of the recycled sample are to be noted in the region of 215 to 220 mm. They are however, difficult to interpret, On the whole, it may be concluded that the dewaxing process leads to little oxidation of double bonds of the abietic acid ring, and apparenty no cyclo-additions of the Diels – Alder type, ring condensations and polymerizations take place[17, 18].

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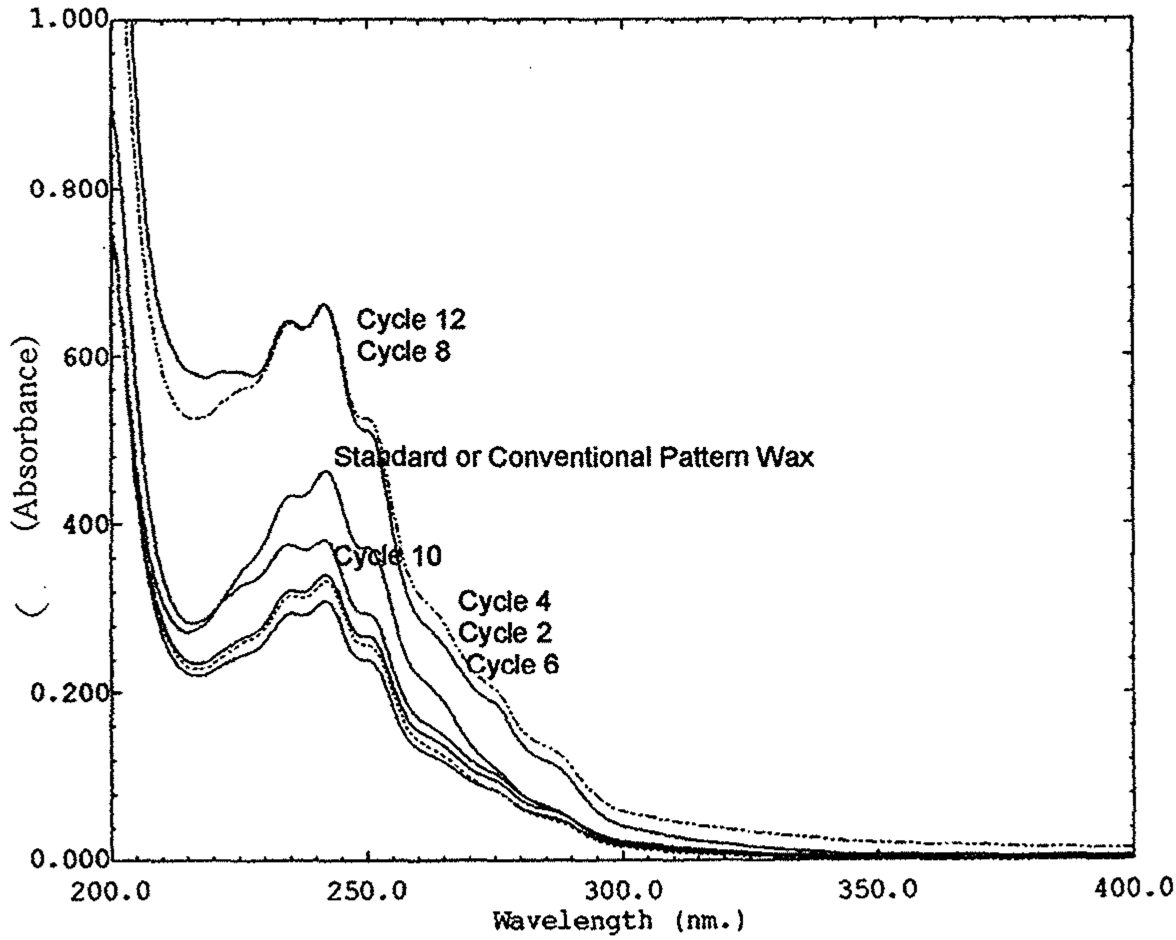

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Figure 5. ilustrates a typical differential scanning calorimetry (DSC) curve for a conventional pattern wax. The two transitions, melting point at 56,2 °C and the flash point at 253,3 are very distinct.

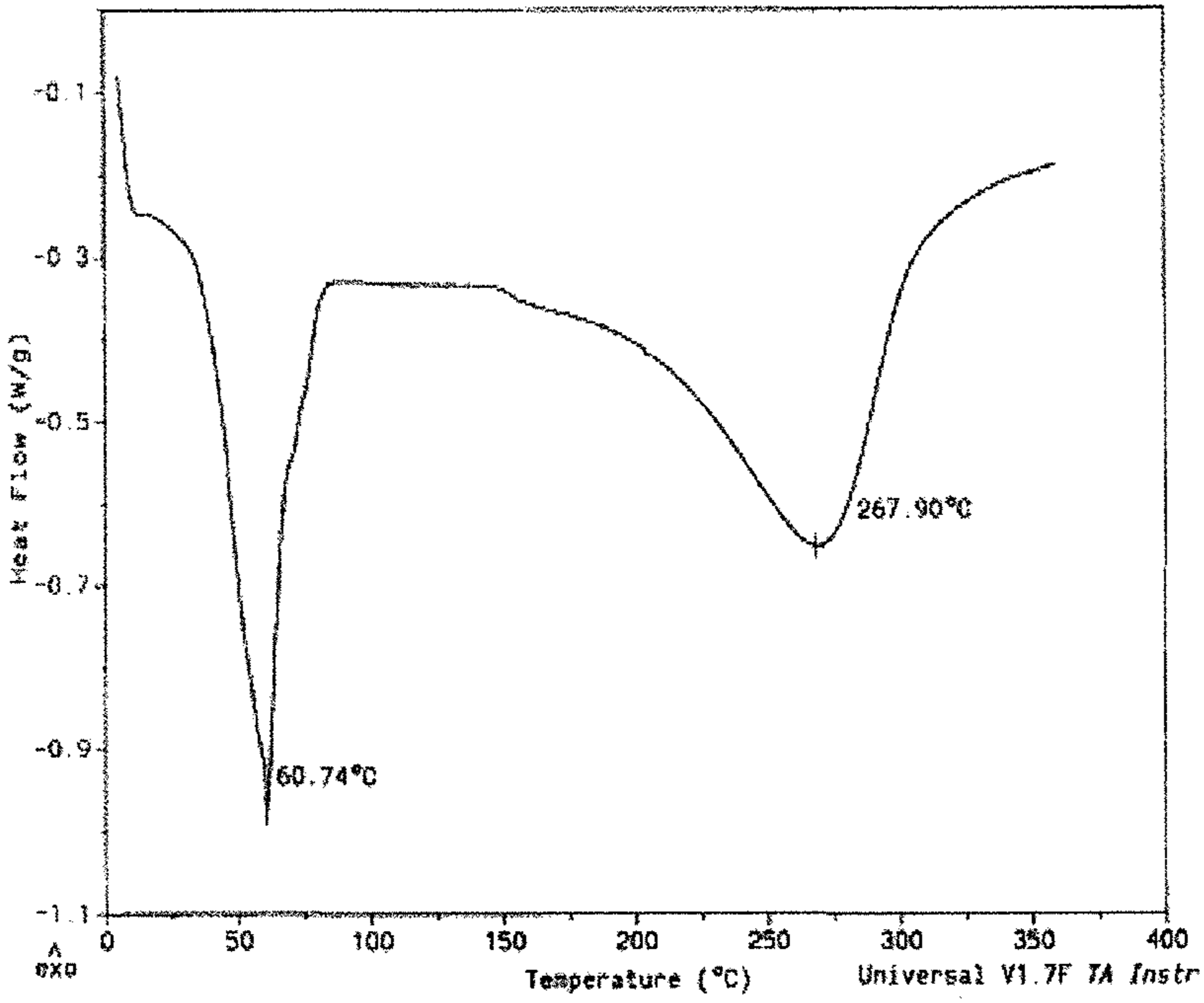

Figure 5. DSC Curve for a Standard Pattern Wax (10 °C/min under N_2 Atmosphere)

Figure 6. shows DSC curves a virgin pattern wax, a dewaxed pattern wax and a dewaxed and dried pattern wax corresponding to the first dried recycling process. Again, the melting and flash points are clearly distinct in all three cases and exhibit essentially the same values. It is interesting to note the presence of a large number of minor peaks for the case of the dewaxed pattern wax indicating the presence of water, essentially in the emulsified and occluded forms. These peaks are absent in the other two cases. Differential Scanning Calorimetry thus appears to be a sensible technique for detecting the presence of water in waxes.

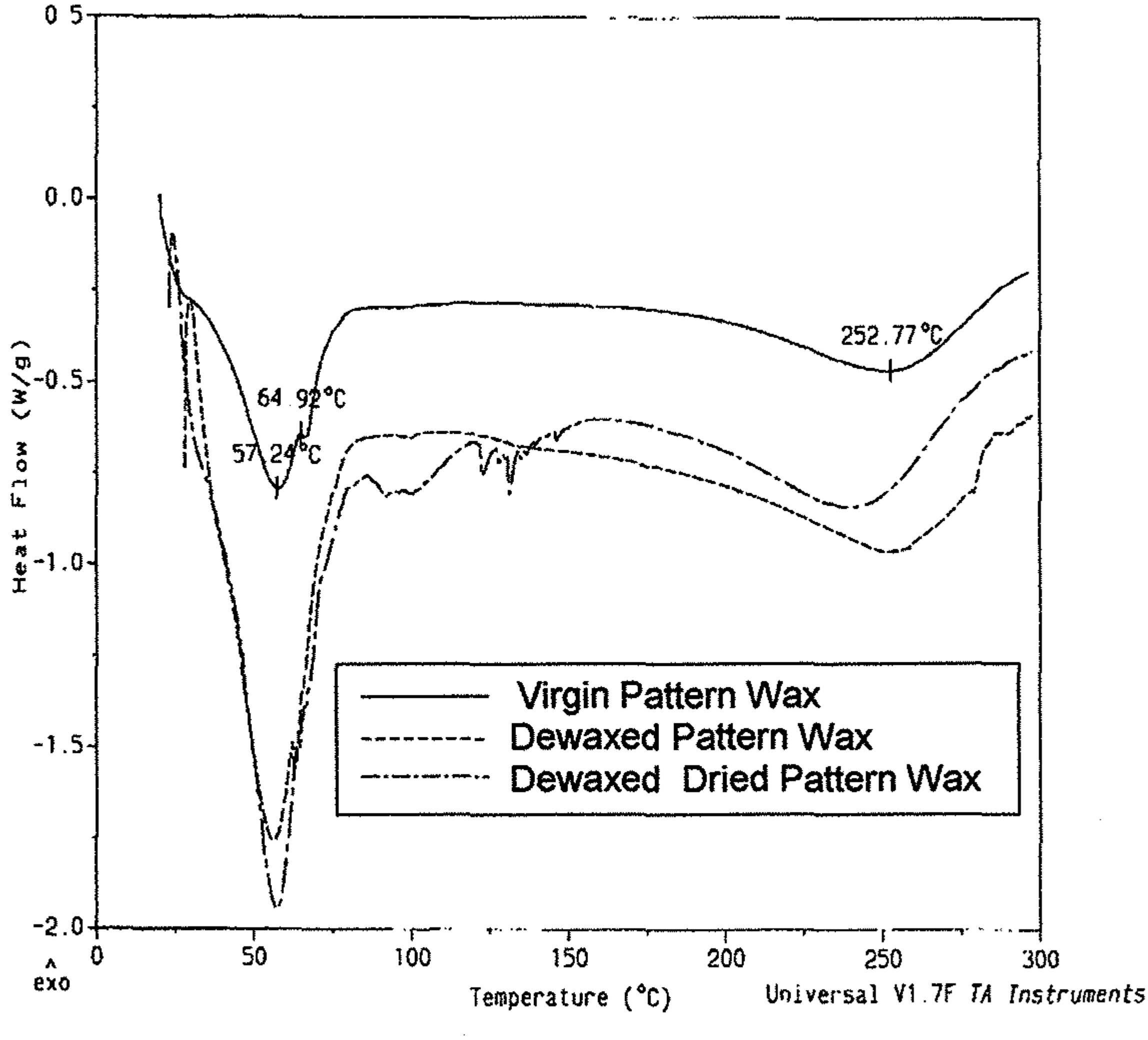

Figure 6. DSC Curves for Virgin Pattern Wax, a Dewaxed Patern Wax and Dewaxed Dried Patern Wax

TG and TGA curves studied the total thermal degradation of pattern wax and representative results are illustrated in Figure 7. The interpretation of the results in terms of TGA and DTA curves leads to three distinct steps. During the first step, below 340 °C (interval A – B) the pattern wax is thermally stable the only processes occurring are melting and loss of humidity. The second step between 340 °C and 470 °C (interval C) involves volatilization and combustion of the fraction of the wax with lower molecular weight. The third step, between 470 °C and 580 °C (interval D) corresponds to the volatilization and combustion of the high molecular weight fraction. The process ends about 600 °C (point E) with total combustion of the wax resulting in an inorganic residue (ashes).

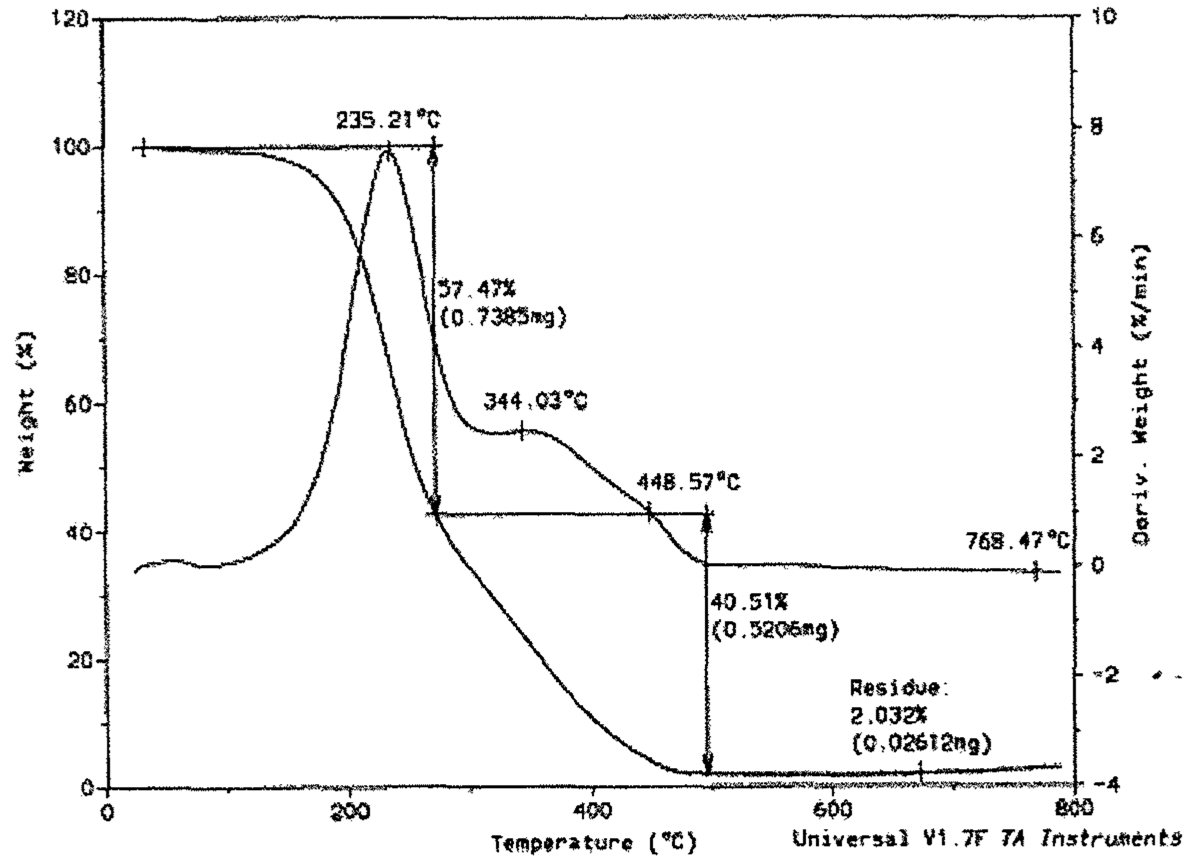

Figure 7. TGA Curve and Its Derivative for a Pattern Wax (Heating Rate 10 °C/min, under Nitrogen Atmosphere).

Table I summarizes the mass loss in percent by weight at different temperatures in the presence of air for pattern wax and some of its components.

Table I. Mass Loss for the Pattern Wax and its Components (%mg) and the Corresponding Temperature in the Presence of Air (40mL/min).

MATERIAL	*Step 1*		*Step 2*		*Step3*	
	°C	Δ%mg	°C	Δ%mg	°C	Δ%mg
Pitch	258,31	83,01		5,98	521,39	10,67
Parafin	263,49	92,63	491,00	7,52	534,75	10,73
Mineral Wax	296,76	77,9	441,57	13,37		
Carnaúba	307,19	64,61	416,94	21,83	495,42	13,62
EVA*	*no mass loss					
Patern Wax	235,21	57,47		40,51		2,03

Analysis of the data in Table I shows that for all the components the preponderant weight loss occurs below 300 °C by volatilization (fumigation) and subsequent combustion of the vapors. The rate of mass loss is an indication of the ease of volatilization and may also show which materials are carried during autoclaving and which may be removed with water. For example, mineral wax is the first to disappear and leaves no residue and thus is easily eliminated and alters the composition and structure of the recycled wax, Carnaúba, on the other hand, volatilized and decomposed more slowly and leaves a lot of residue.

The behavior of pattern wax is different when compared to its components, showing that it is really a blend. The study of the degradation process under oxidizing atmosphere may provide a wealth of information about the reactivity, heats of reaction, kinetics and activation energy of the steps involved.

Figure 8 illustrates some typical Shore D Hardness values obtained for standard pattern wax and the corresponding 12 cycles simulated with and without the presence of ceramic investment at 23 °C.

Similar results are presented in Figure 9 for reformulated pattern wax at 23 °C for the odd numbered cycles simulated.

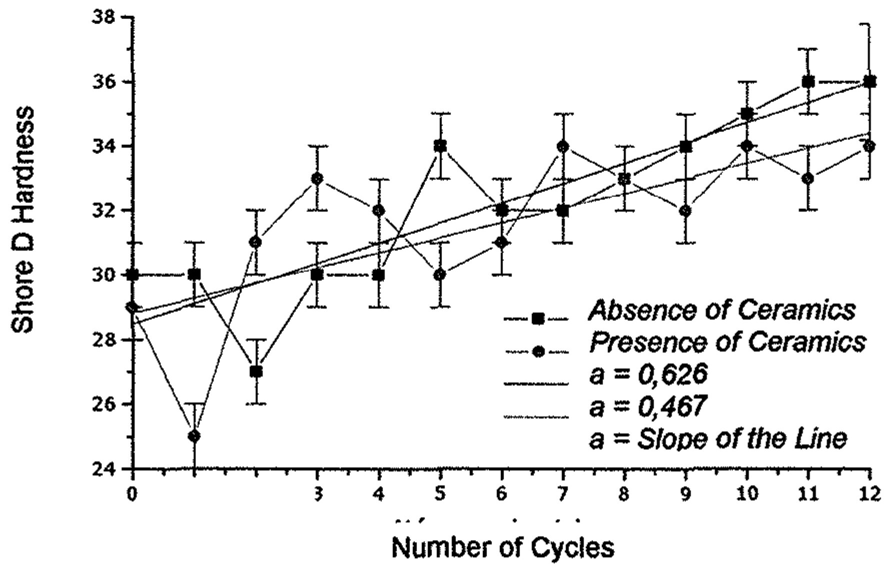

Figure 8. Shore D Hardness for Patter Wax in the Presence and Absence of Ceramics for Twelve Simulated Cycles.

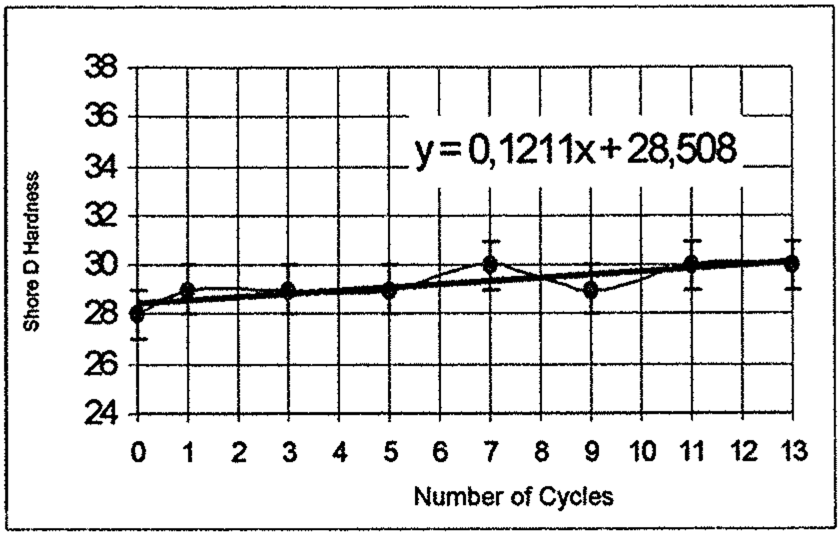

Figure 9. Shore D Hardness for Reformulated Pattern Wax at 23°C for Odd-numbered Cycles Simulated.

The hardness increases in a linear form for samples with or without the presence of ceramics. The slope "a" of the line in Figure 8 may be considered a measure of the degradation of the wax during recycling. The experimental results in all cases sugest a relative small degradation rate and relative structural instability for each cycle.

Similar results are presented for the refractive index of the pattern wax and reformulated pattern wax in Figures 10 and 11, respectively, at 80 °C. As can be seen, the refractive index increases both in the presence and absence of ceramics.

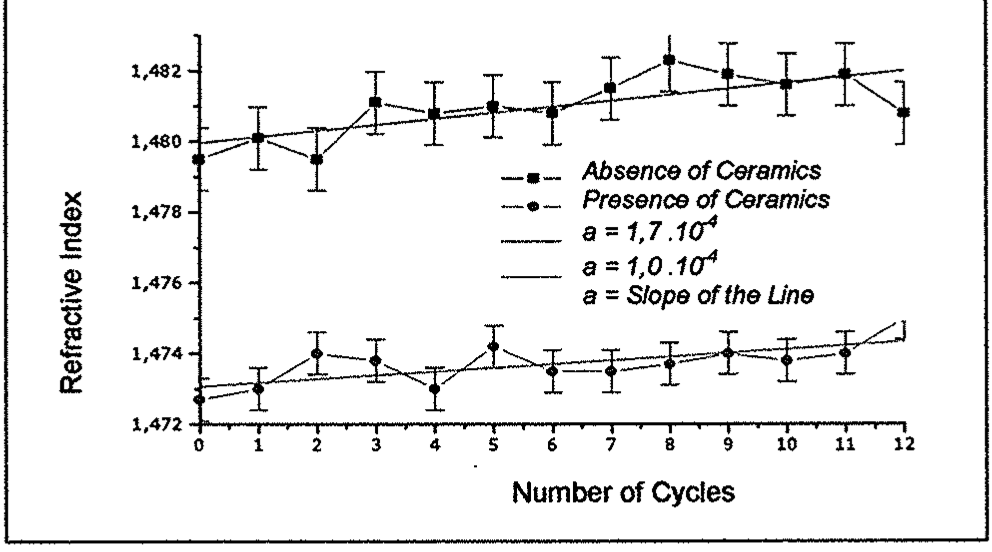

Figure 10. Refractive of Pattern Wax and 80 °C in the Presence and Absence of Ceramics.

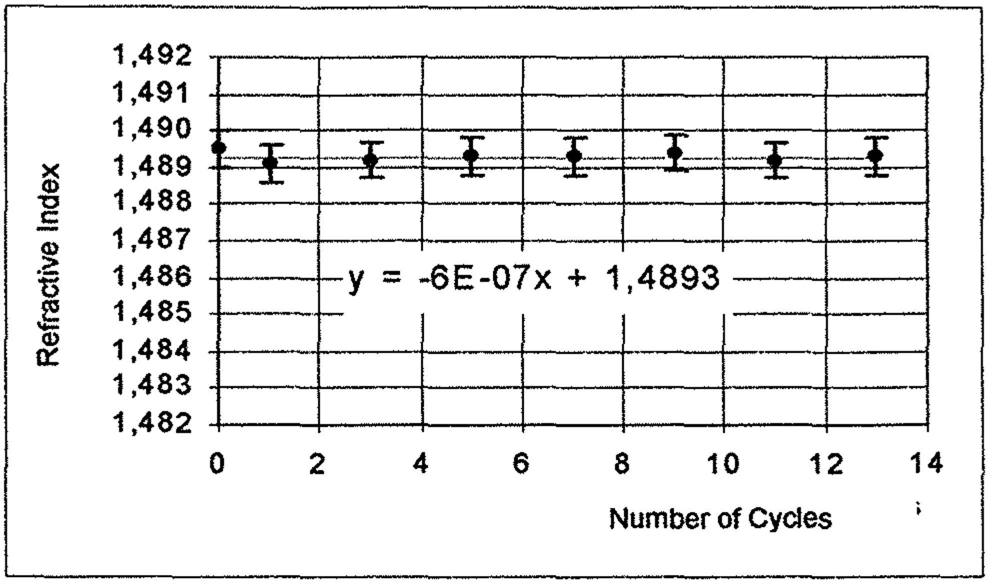

Figure 11. Refractive Index of Reformulated Pattern Wax at 80 °C for Odd-Numbered Simulated Cycles.

The presence of fine ceramic particles decreases as a whole the refractive index as can be seen in Figure 10. Again, the gradual increase of the refractive index as a function of recycling is indicative of a slow and linear degradation of the wax and its structural instability, since the refractive index is directly related to molecular composition.[20]

Volumetric expansion, water content and the modulus of elasticity are not good parameters for determining degradation or decomposition of the wax. On the other hand, they are very sensitive to structural instability, as can be deduced from the results of the recycling processes.

In conclusion it may be stated that the original standard pattern wax and the reformulated pattern wax are heterogeneous dispersions. Pitch added in a high concentration tends to segregate the system causing instability of the mixture.

Wax has typical and reproductive spectra that may be used for its characterization. In the infrared (IR), bands at 2907, 1469 and 717 cm^{-1} are characteristic of paraffin and mineral waxes due to hydrocarbons, the acid fraction has bands at 2907, 1694 and 1277 cm^{-1} and the ester fraction exhibits strong peaks at 3426, 1694 and 1181 cm^{-1}. In the ultraviolet (UV) region there is a strong band at 241 mm characteristc of abietic acid present in pitch.

Differential Scanning Calorimetry (DSC) termal curves for pattern wax are typical and show that the processes occurring below 300 °C are loss of humidity and volatile materials, fusion, fumigation (volatization of inflammable vapors and incipient oxidations. The thermogravimetric (CTG) curves obtained for total thermal degradation indicate that wax contains two characteristic molecular fractions, one that volatilizes and oxidizes between 340 and 470 °C and a second one that undergoes similar processes between 470 and 580 °C. The hot water present in the autoclave mixes with the wax and upon solidification most of it remains occluded in the mixture and the rest is emulsified, beeing associated with polar groups of the wax.

The experimental results obtained for the analysis of sample of pattern wax subject to the simulated recycling show that the main change is random and of a structural nature and that the extent of degradation is very small and can be measured by the refractive index, hardness, viscosity and other dynamical and mechanical parameters.

The shift of the base line of DSC curves indicates that the thermal properties of the wax are changed during the recycling. The change may be due to oxidations and elimination of components by volatilization and carriage.

The infrared spectra show the possible occurrence of cleavage of molecules, oxidations, dehydrogenations, reactions involving functional groups, ring condensations and formation of a new products. Similar processes appear to take place with pitch during dewaxing especially involving dimerization of acid isomers, ring condesantions and double bond oxidations.

The higher homogeneity of the dewaxed wax samples containing ceramics is due to the successive processing steps (filtration, dewaxing and removal of the water during each cycle) that eliminate the incompatible fractions and due to the presence of fine ceramic particles, that improve the structural stability of the wax.

The reformulated pattern wax presented all the prerequisites necessary for sucessful recycling and possible industrial use or application.

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