Wax emulsions in aqueous polymeric coatings: contributions and mechanisms

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ABSTRACT *Three different wax emulsions were mixed into both a polyvinylidene chloride latex and a styrenated acrylic latex. Surface properties of these coating mixes on paper were evaluated as to the effect of wax concentration on coefficient of friction (COF), pick temperature, gloss, and wetting tension; the effect of post-cure on the COF and wetting tension; and the effect of cure temperature on COF. Using the proper amount of the correct wax emulsion will enhance the properties of water-based polymeric coatings. Three mechanisms are submitted for explaining the results: the ball bearing, the bloom, and surface continuity theories.*

KEYWORDS
Antiblocking
Coefficient of friction
Cure temperature
Gloss
Pick temperature
Post cure
Printability
Slip
Wetting tension

Wax emulsions have been used extensively in aqueous polymeric coatings for many years. These emulsions can be easily incorporated into the formulation. The mix of emulsion and coating is stable against the tendency to separate into phases. Important benefits to the coated substrate are:

- Lower coefficient of friction
- Antiblocking
- Improved rub resistance
- Increased barrier properties
- Controlled release
- Better machinability
- Greater lubricity.

All of these properties (with the possible exception of barrier properties) appear to be surface phenomena. Our purpose was to verify and quantify some of these effects and determine a mechanism by which wax emulsions impart these special characteristics to the surface.

Waxes and wax emulsions

The properties of waxes that have the greatest impact on performance and usability in aqueous coatings are:

- Chemical composition
- Molecular weight
- FDA acceptability
- Melting point
- Hardness.

Carnauba wax, a high-molecular-weight ester, seems to fit many of these characteristics required of a slip and antiblock additive. Carnauba wax has a melting point of 85°C, a temperature at which many coatings can be easily cured. Furthermore, it is extremely hard and is GRAS listed.

For our study, we considered the important aspects of wax emulsions to be:

- Wax type
- Emulsifier-type/compatibility
- Total solids content
- Particle size/optics
- FDA acceptability
- Stability.

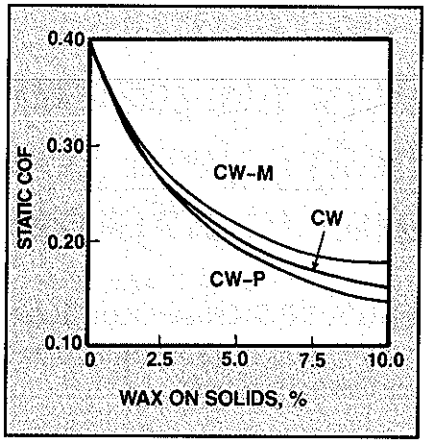
The type of wax used is the most critical choice because some waxes are more effective than others (*1–3*). The emulsifier type chosen to make the wax emulsion will determine the compatibility with the latex with which it is mixed. A wax particle size that is too large will detract from the coating gloss, whereas a particle size that is too small can result in poor antiblock. If the coating is intended for food contact use, the ingredients must be acceptable under FDA Section 21 CFR 176.170, 175.300, or 175.320, etc.

The stability of the wax emulsion will also determine its suitability for a specific latex system. For instance, if the system is expected to be stable to acid, the wax emulsion should be insensitive to low pH. If it is likely to be held in storage, the wax emulsion should resist phase separation and spoilage from bacteria. If it could be exposed to freezing temperatures or excessive heat, the wax components

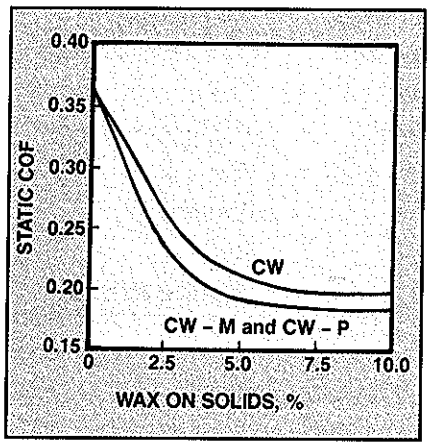
I. Wax emulsions tested

Wax type(s)	Abbreviation	Melting point °C	Melting point °F
Carnauba wax	CW	85	30
Carnauba and paraffin	CW-P	85/64	30/147
Carnauba and microcrystalline	CW-M	85/92	30/198

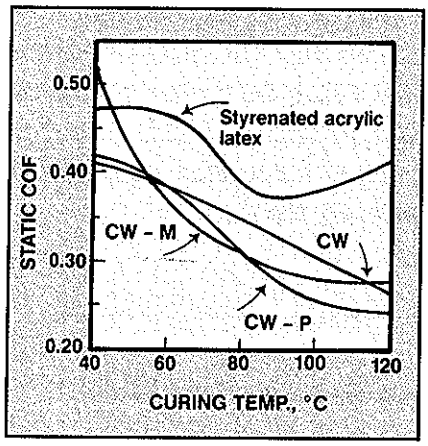
1. Static COF vs. wax concentration in styrenated acrylic latex (Cured for 20 s at 110° C)



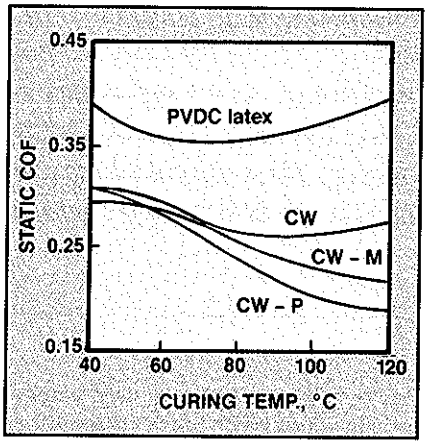
2. Static COF vs. wax concentration in PVDC (Cured for 20 s at 110° C)



3. Static COF vs. curing temperature, 3% wax on styrenated acrylate (Cured for 20 s)



4. Static COF vs. curing temperature, 3% wax on PVDC (Cured for 20 s)



need to be stable against temperature extremes. Furthermore, the wax emulsion may have to stand up under extensive pumping and mixing, or it may have to retain its integrity against electrolytes, cosolvents, pigments, or other emulsifiers.

Surface tests and results

We chose three different wax emulsions for this study. These are given in **Table I**. All three contained the same anionic emulsifier. The latices selected were a commercially available styrenated acrylic and a polyvinylidene chloride latex (PVDC). The wax emulsions were incorporated into both of these polymers at concentrations ranging from 0% to 10% wax solids on polymer solids. All coating mixes were adjusted to 40% total solids content.

The coatings were allowed to age for 24 h prior to being applied to a commercially available, 30-lb glassine paper using a No. 3 Meyer Rod. The coated samples were cured according to the experiment and were allowed to age for 24 h at room temperature before testing.

The surface properties of these coating mixes were evaluated as to the effects of wax concentration, post-cure, and cure temperature on the coefficient of friction; the effect of wax concentration on pick temperature and gloss; and the effect of wax concentration and post-cure on wetting tension.

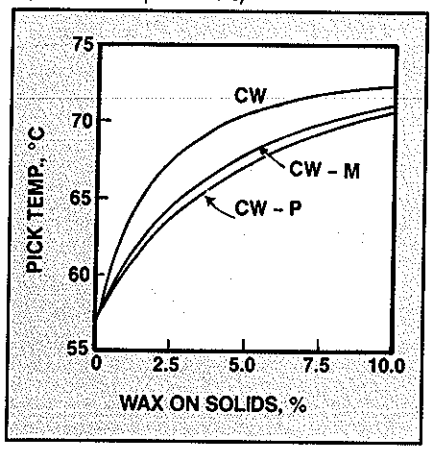
Coefficient of friction and wax concentration

Figures 1 and 2 indicate what has been found in actual production—a fairly steep response to wax addition between 0% and 4% solids on polymer solids, with the effect diminishing after 4%. This dramatic reduction in coefficient of friction at low wax concentrations accounts for the widespread use of wax emulsions in latex systems. All waxes studied gave approximately the same response in coefficient of friction with varying concentrations of wax.

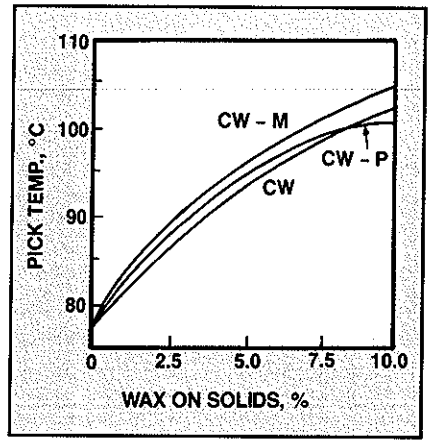
Coefficient of friction and curing temperature

Previous work with waxes in a solvent-based system indicated that the curing temperature of the coating has a considerable impact on surface properties (*2*). Our studies of wax additives in water-based coatings support these findings. We selected the coefficient of friction as a criterion for measuring the behavior of a wax in latex because it is a reasonable quantitative indication of surface effects. Glover, in his studies of slip agents in extruded polyethylene, also used the coefficient

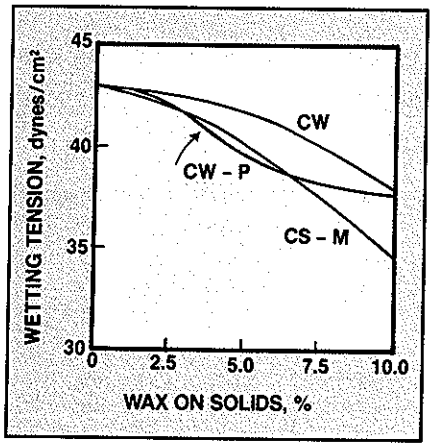
5. Pick temperature vs. wax concentration in styrenated acrylic latex (Cured for 20 s at 110° C; tested at 30 psi for 2.5 s)



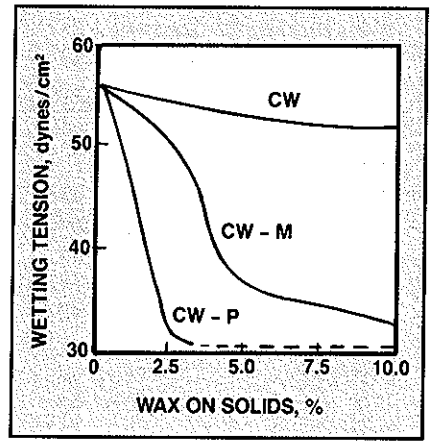
6. Pick temperature vs. wax concentration in PVDC (Cured for 20 s at 110° C; tested at 30 psi for 2.5 s)



7. Wetting tension vs. wax concentration in styrenated acrylic latex (Cured for 20 s at 110° C; aged 2 weeks at RT)



8. Wetting tension vs. wax concentration in PVDC (Cured for 20 s at 110° C; aged 2 weeks at RT)



of friction to measure wax migration (*3*). We chose to use 3% wax solids on polymer solids because this appears to be the most efficient usage level.

Figures 3 and 4 demonstrate that there is the pronounced effect of curing temperature on the coefficient of friction for both latices. It is necessary to approach or exceed the melting point of the wax (>80°C) to obtain the full benefit of the wax additive. However, as opposed to the results of the previous tests, the three wax emulsions demonstrated slightly different responses. The best explanation for these differences is that the lower melting point components in the carnauba/paraffin mixture give it more mobility at lower temperature.

The effect of post-cure on coefficient of friction

The effect of aging the coated substrate at ambient conditions on COF was divided into short-term and long-term studies. Wax emulsions at 3% solids on polymer solids were mixed into the styrenated acrylic and PVDC latex, coated onto glassine paper, and cured for 20 s at 110°C. The coefficient of friction was first measured over a 93-day span in increments of approximately five days. There was little measurable response to long-term curing, regardless of the wax or the latex used.

To measure the short-term effect of curing on the coefficient of friction, the same conditions were employed, except that the coefficient of friction was measured hourly over a 24-h period. The results were quite surprising. The behavior of the coefficient of friction vs. time was erratic, but it leveled off after about 13 h. Besides, the coefficient of friction for the polymer with no wax also gave us erratic readings, which may account for the problem in measuring the response to wax content. In any event, these experiments indicate that it is necessary to allow a coating to age for at least 13 h before measuring its surface properties.

The effect of wax concentration on pick temperature

The advantage of using wax emulsions in aqueous polymeric coatings was again demonstrated when a large increase in pick temperature as a function of wax concentration was observed (**Figs. 5 and 6**). For this investigation, coated samples containing various levels of wax were placed on a Sentinel Heat Sealer, and the temperature at which picking occurred was recorded. Most of the waxes behaved in a similar manner, but the effectiveness of wax at low concentrations was quite impressive.

The effect of wax concentration on gloss

It has been said occasionally that wax emulsions can detract from the gloss of a coating. However, we did not find this to be the case for the three wax emulsions and the two latices used in this study at the concentrations tested. Nevertheless, based on commercial experience, it is necessary to select a compatible latex and wax emulsion combination to maintain gloss.

The effect of wax concentration and post-cure on wetting tensions

Experiments to determine the effects of wax concentration and post-cure on wetting tension were performed. These experiments were intended to give us an indication of how wax would affect further converting, such as printing of the coated substrate. The test method used was ASTM D 2578 (American Society for Testing and Materials). This test, "Wetting Tension of Polyethylene and Polypropylene Films," involves preparing solutions of ethyl cellosolve and formamide and applying these solutions to the coated substrate.

Figures 7 and 8 and **Table II** show, for the first time, an appreciable differentiation of the wax emulsions in at least one latex. The carnauba wax emulsions at less than 4% had little effect on the wetting tension in either latex. Thus, coatings containing this type of wax emulsion should be as printable as the polymer itself. The carnauba wax/paraffin and the car-

nauba/microcrystalline wax blends also seemed quite usable in a styrenated acrylic at low concentrations. However, these same two emulsions in PVDC lowered the wetting tension so much that printing could be problematic. It was no surprise to find that the wetting tension of the wax emulsions themselves followed this same trend.

Another interesting result was that on aging, the coated paper sometimes did and sometimes did not show a decrease in wetting tension (Table II). For instance, the carnauba wax emulsion showed no change in wetting tension over a two-week period with PVDC, but a definite measurable change was evident with the styrenated acrylic latex. On the other hand, the carnauba wax/paraffin emulsion showed a decrease in wetting tension with time in PVDC but not in the styrenated acrylic latex. The carnauba/microcrystalline wax emulsion showed a slight decrease in wetting tension in the PVDC latex but considerably more wetting tension in the styrenated acrylic latex. Currently, no explanation is offered for this behavior.

II. Wetting tension as a function of time and wax concentration

	Wetting tension, dynes/cm²			
	1 h	*1 day*	*1 week*	*2 weeks*
	PVDC latex			
Polymer only	56	56	56	56
Carnauba wax				
1.5% solids	56	55	55	55
3.0% solids	54	55	54	54
5.0% solids	54	56	54	53
8.0% solids	52	55	52	52
10.0% solids	52	56	52	52
Carnauba/paraffin				
1.5% solids	47	45	43	43
3.0% solids	34	32	31.5	30
5.0% solids	33.5	<30	<30	<30
8.0% solids	33	<30	<30	<30
10.0% solids	33	<30	<30	<30
Carnauba/microcrystalline				
1.5% solids	56	56	55	54
3.0% solids	52	54	54	53
5.0% solids	36	35	36.5	36
8.0% solids	36	33	35	34
10.0% solids	35	32.5	33	32.5
	Styrenated acrylic latex			
Polymer only	45	44	43	43
Carnauba wax				
1.5% solids	45	43.5	43	42.5
3.0% solids	44	43	43	42
5.0% solids	44	43	43	42
8.0% solids	43.5	43	40.5	40
10.0% solids	43	43	39	38
Carnauba/paraffin				
1.5% solids	44	44	43	43
3.0% solids	42	42	42	42
5.0% solids	37	36	36	35.5
8.0% solids	37	36	36	35.5
10.0% solids	35	34	33.5	34
Carnauba/microcrystalline				
1.5% solids	45	43	42.5	42.5
3.0% solids	44.5	44	41.5	41
5.0% solids	43	42	41	41
8.0% solids	40.5	39	38	37
10.0% solids	39	36	34	33

Mechanisms

When this study was started, two theories prevailed as to the possible mechanisms by which we might explain our results—the "ball bearing" theory and the "bloom" theory. The surface continuity theory is a newly proposed explanation.

Ball bearing theory

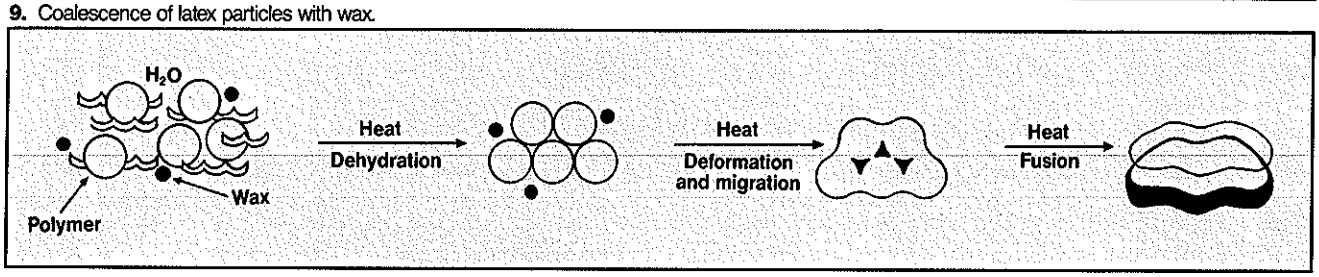
In the ball bearing theory, we envision a coated surface with particles of wax protruding and preventing another surface from making good contact. This theory would easily explain most of the surface phenomena measured, except for (a) the decrease in the coefficient of friction with increasing curing temperature and (b) the decrease in wetting tension with aging.

Bloom theory

At the time our tests were completed, the only way to explain *all* of the laboratory and commercial results was to suggest that the wax was somehow able to migrate (or "bloom") to the surface with the aid of heat or over a period of time. In 1965, Roth (*2*) performed some experiments with a solvent-based system on cellophane. The results indicated that carnauba wax was able to almost double its concentration in the upper 1 μm of a 4-μm-thick coating with the application of heat. Candelilla wax showed a threefold increase in surface concentration. The only way to explain these results was to suggest a wax migration to the surface. Roth measured the surface wax concentration by SEM and infrared techniques. Glover's work on slip additives in extruded low-density polyethylene (LDPE) also supported the migration theory (*3*).

It was postulated that the same phenomenon could occur in an aqueous system using a model based on the coalescence of latex particles (**Fig. 9**). Spheres of polymer particles are first packed together as the water evaporates, leaving voids between the spheres. More heat causes a deformation of these particles. If enough heat is applied, continuous film formation is achieved. However, because this coalescence process is in all likelihood imperfect, thermoplastic wax particles,

9. Coalescence of latex particles with wax.



III. Effect of drying conditions on surface wax concentration by ATR

Actual wax incorporated, %	*Wax in upper 25% layer, %*	
	24 h at RT	*1 min at 100°C*
3.0	2.9	3.1
4.0	4.2	3.7
5.0	5.1	4.5
6.0	6.0	6.0
8.0	8.0	7.4
9.0	9.3	9.4
10.0	9.9	10.3

RT = room temperature

which have a low melting point, are allowed to melt and flow into the interstices and migrate, or bloom, to the free surface through the voids. The "bloom" theory, because it is dependent on time and temperature, did explain all of the surface effects observed, including the decrease in the coefficient of friction with heat and the decrease in wetting tension with time. Even now, the bloom theory is the only way to explain some results that are beyond the scope of this paper.

The old theories and new experimental results

We set out to measure surface wax concentration to determine which of these two earlier theories was correct. Samples of coated glassine paper were prepared using known ratios of carnauba wax in PVDC. Dried at *room temperature* for 24 h, these samples were analyzed on a Nicolet 5 DXC FTIR using attenuated total reflectance (ATR) to a depth of 25% of the total coating thickness. Using Nicolet's PLS Quant software, we compared spectroscopically determined wax content in the top 25% of the coating vs. actual carnauba wax content. The comparison yielded a curve with a correlation coefficient of 0.998, indicating that the technique was accurate.

Coated samples ranging from 3% to 10% carnauba wax on PVDC solids were then prepared but were *heated* to 110°C for 1 min and aged overnight. If carnauba wax was able to migrate to the surface by the application of heat, then we could expect to find a larger percentage of wax on the surface than the percentage at which the wax was incorporated into the mix. Surprisingly, minimal deviation was found, as shown in **Table V**. Thus, there was no evidence of bloom with heat!

This entire procedure relied on the assumption that, since the samples were dried at room temperature, no migration occurred in the preparation of the calibration curve. To verify this assumption, a wet sample containing 6% carnauba wax solids on PVDC solids was dried at room temperature for 72 h on a horizontal ATR unit. This procedure allows us to evaluate the *bottom* 25% of a sample. If migration occurs, this section should have a depleted percentage of wax. (The assumption here is that there is no downward migration, which is not an unrealistic approach, given the difference in specific gravities of the wax and PVDC, as well as the fact that Glover (*3*) found no migration towards nonporous substrates.) We found a value of 5.4% for carnauba wax, which is in good agreement with the expected value of 6%. This finding, then, would validate the assumption that little or no migration takes place with room temperature curing and for the systems evaluated, no wax migration to the surface occurs with or without heat.

Surface continuity theory

If no bloom occurs, there must be another explanation for the surface properties exhibited by latex systems incorporating wax. The newly proposed concept is the "surface continuity" theory. It is quite possible that once the coating has dried, the wax particles are "frozen" in place, and those particles on the surface of the coating are the only ones with enough freedom to flow with the application of heat. As the curing temperature is raised, the surface wax melts and levels out over the free surface, burying the polymer and minimizing its contribution to the surface properties of the coating. As a result, the wax has not increased its concentration on the surface but has merely become more efficient. This theory does explain all of the results and is supported by our re-examination of the SEMs made by Roth (*2*).

This discovery does not necessarily refute the work of Roth and Glover. Roth performed his studies in THF, and Glover worked in LDPE, both of which are quite dissimilar from the water-based systems we studied.

Conclusions

Wax emulsions at low concentrations are extremely useful in modifying polymeric coatings to obtain good slip and antiblock properties without having to sacrifice other qualities such as gloss and printability. Which mechanism explains these findings best? The answer is still uncertain, but formulators now have some models to use to predict results instead having to rely on the trial-and-error methods of the past.□

Literature cited

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