2001 Technical Focus Lecture

Meeting the Challenge of FORMULATING FOR THE FUTURE

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The history of the paint market shows that change quickly follows new technical advances or governmental regulation. Restrictions on the use of volatile organic compounds (VOCs) in architectural coatings are no exception. This paper examines the history of VOC regulations and resin technology in Europe compared to the U.S. Despite differences in formulations, substrates, and test methods, there are lessons that can be applied by U.S. paint makers and their suppliers. Other new directions in polymer synthesis and technology which may impact the paint industry are also discussed.

INTRODUCTION

The history of coatings technology is full of change—from new resin technology to pigments, application, and manufacturing methods. The industry adapts quickly to advances in technology and restrictions on raw materials. The current climate of increasing restriction on the use of volatile organic compounds (VOCs) is one more chapter in this history. Regional differences in substrates, formulations, and legislation have led to a great variety of options for learning how to respond to this challenge.

HISTORY

Any history of painting usually starts with the famous cave paintings of Europe. The focus of this paper will be the 20th Century, which saw a tremendous amount of change in nearly every facet of the coatings industry. Three segments will be presented: paint process and supply, pigments, and resin technology.

Process

Until the mid- to late 1800s, paint was typically made by professional painters—craftsmen who both prepared paint and applied it. Most paint was prepared on site. Interior surfaces were often coated with whitewash, distempers, or casein paints which had either no binder at all, or binders such as animal glue or casein which had poor durability. Casein paints remained popular into the 20th Century, purchased as powders to be mixed with water just before use. Some are still available commercially. Exterior paints were made by mixing white lead paste into linseed oil.[1] Lead functioned both as white pigment and as drying agent for curing of the linseed oil. This combination was state-of-the art for durable exterior paint for centuries as it had good waterproofing qualities and failed by a slow chalking process. It found no substitute until the advent of rutile TiO_2 and acrylic latex.

The industrial revolution brought about centralized manufacturing of paint dispersions as well as the production of a variety of resin technologies. The first patent for "ready mixed paints" in the U.S. was granted in 1867.[2] Sales began in earnest in the mid-1880s and paint factories proliferated. By 1900 nearly 20 million gallons per year of ready mixed paint were sold in the U.S., and this volume rose steadily. Serious study of exterior durability of paints was reflected by the construction of the first "test fence" specifically for this purpose at North Dakota State University in 1906.[3] This major shift—the birth, really, of the industry in its present form—demonstrates how quickly technological advances can become accepted and established.

Pigments

In the 1800s lead was used extensively despite its known toxicity. Other extenders were also used, including calcium, silicon, and barium sulfate.[4] Zinc oxide was identified as a replacement for lead white in the 1780s. It began to be mass produced about 1850, making it economically feasible to use, and gave better hiding power than lead. Problems with storage stability prevented zinc oxide from fully displacing lead. Lithopone—a mixture of zinc sulfide and barium sulfate—was introduced in 1874. Its hiding power is greater than zinc white. By 1930, lithopone and zinc oxide had mostly replaced lead for interior paints; lead was still used extensively for exterior paints and metal coatings.

The first titanium dioxide pigments were introduced in the 1930s. The early versions were mainly anatase in crystal form, and catalyzed the breakdown of paint films.[1] Exterior paints for a time were intentionally formulated with a fraction of anatase TiO_2 as "self cleaning paints," for a small amount of chalking allows dirt to be removed by rain. Rutile TiO_2 was commercialized after World War II and finally allowed the formulation of durable paints that do not contain lead.

Once again, an advance in technology—in this case the production of rutile TiO_2—very quickly was adopted as standard for industry and largely displaced previous practice—without regulation. The gradual nature of the replacement, however, illustrates that

Presented at the 78th FSCT Annual Meeting, November 5, 2001, in Atlanta, GA.
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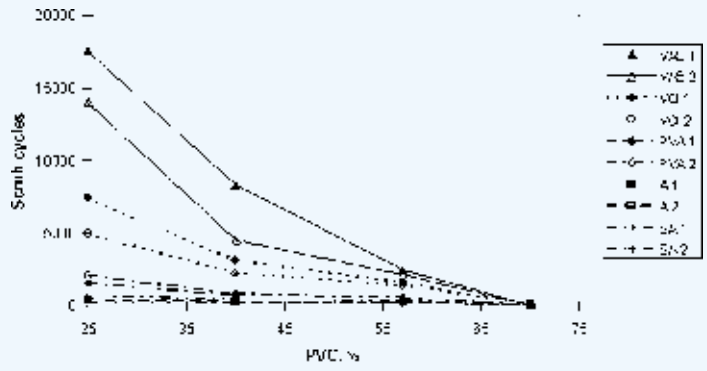

Figure 1—Scrub vs. PVC for a variety of latex types.

good performance needs to be demonstrated before conversion can occur.

Resins

Resin technology was entering a period of great development starting in the mid-1800s, but adoption of these new technologies into the architectural paint industry was slow. Industrial finishes such as cellulose nitrate for automotive coatings were being developed, as were resins for the infant plastics industry.

Resin technology for architectural coatings took a leap forward with the introduction of alkyd resins in 1927.[4] This resulted from the invention of glyptal resins, reaction products of glycerol and phthalic anhydride used as adhesives. They were too brittle to be used in coatings, but modification with fatty acids made them suitable.[5] Alkyds proved to be vastly superior to linseed oil especially after continued improvements during the 1940s and 1950s. The European paint industry rapidly moved from simple oil-based paints to alkyds while the U.S. was slower to move.[1]

Synthetic latex production was commercially driven by war efforts to find replacements for natural rubber. A postwar outgrowth of this work found tremendous interest in the U.S. for styrene butadiene rubber (SBR) dispersions for their utility in water-based latex paint. The first SBR was sold into architectural coatings application in 1948.[6] Consumer desire for easy cleanup and new roller technology combined to make a rapid market shift. Sales of SBR latex increased extremely quickly, with 33% of solvent-based interior paints replaced by latex paint within four years of its introduction in 1948.[1] This is one of the clearest examples of the rapidity with which the market has responded to technological advance.

SBR was gradually replaced by other latex chemistries during the 1950s and 1960s. The deficiencies of SBR that account for this shift include color stability and chalking.[6] Styrene acrylics were introduced in 1953 to address some of these issues; current styrene acrylics are often sold as "modified acrylics" even though they may contain as much as 50% by weight styrene.

During the 1950s and 1960s, a wide range of chemistries was introduced: vinyl acrylic, vinyl chloride, vinyl acetate/ethylene, etc. It seems that from this point the markets developed very differently in the U.S. and Europe. These differences were most likely driven by differences in formulation, substrates, and testing methods.

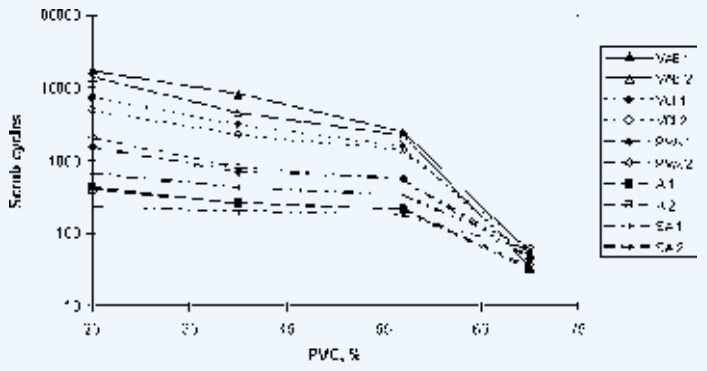

Figure 2—Scrub vs. PVC for a variety of latex types.

Poly(vinyl acetate) homopolymer emulsions began to be used in paints before WWII, with one British company founded in 1939 for PVAc manufacture. After the war, development of vinyl acetate based resins continued in Western Europe. The high T_g of PVAc homopolymer made the use of plasticizer necessary. The superior colorfastness and yellowing resistance of vinyl acetate based resins helped drive the market in Europe away from SBR.

Over the next 20 years latex-based paints captured nearly the entire European interior paint market and much of the exterior masonry paint market. Copolymers of vinyl acetate with acrylates, versatate, and ethylene reduced the necessity for plasticizer and enhanced performance in terms of alkali resistance, scrub, etc.[1]

The development of vinyl acetate-based latex in the U.S. seemingly lagged behind that in Europe. Vinyl acrylics became a force in the U.S. market in the 1950s. VAEs, introduced in the late 1960s or 1970s, tended to be used mainly in flat paints. Their typical T_g of 0 to 5°C resulted in excellent film formation, durability, and scrub resistance, but unacceptable blocking performance in semigloss and satin paints. Vinyl acrylics with somewhat higher T_gs tended to be more versatile in their ability to be used across a wide range of PVC, with the use of coalescing solvents. The market share for VAEs is increasing as VOC regulations increase and as low odor and environmentally friendly paints are finding more acceptance, since they require little to no solvent to form good films with high performance.

All acrylic paint resins were developed commercially in the 1960s. They soon proved extremely popular as they demonstrated excellent exterior durability. Semigloss paints based on acrylic resins are popular in the U.S. for good wet adhesion and block resistance. "Low VOC" vinyl acrylics have recently been introduced as another option for formulating at low solvent levels. These products typically have significantly higher levels of butyl acrylate than traditional or high scrub vinyl acrylics in order to reduce T_g.

CURRENT MARKET

Significant differences exist between the U.S. and EU markets in formula-

tions, substrates, and performance standards. One good example is the PVC for interior flat paint formulations. A high quality interior flat paint in the EU has a PVC of 65-75%, while a low priced paint may go as high as 85%. In contrast, in the U.S., a high quality interior flat paint will have a PVC of 57-60%, and the highest PVC typically seen is roughly 70%.

This difference is likely due to several factors. Customer preference in the EU seems to be for more frequent repainting and expectations for durability are lower. EU test methods for scrub resistance use less severe conditions (nonabrasive media) and so higher PVC paints are able to qualify for "scrubable" designations. This choice of formulation also helps drive choice of resin, as relative performance of various resin types is quite different at such high PVCs.

To illustrate this point, the following figures show the scrub performance for a PVC ladder using a number of different binders. Two each of various chemistries were tested: vinyl acrylic (PVA), acrylic (A), vinyl acetate/ethylene (VAE), styrene acrylic (SA), and ethylene/vinyl chlorides (VCl) with or without vinyl acetate. A typical high quality flat interior paint grind was made including a variety of extender pigments. The PVC was adjusted from 25-70 using the same grind, so that the relative amounts of TiO_2 and extenders were constant and the amount of binder varied. This results in a very impractical paint, as the low PVC paint had poor hiding while the highest PVC paint contained more TiO_2 than would be used commercially. Varying the PVC in this way did keep the effects of binder and pigment interface relatively constant. Formulations are attached in *Appendix* A.

Figure 1 shows the number of scrub cycles versus the PVC using ASTM D 2486. The wide range of response at the lowest PVC (from 200 for styrene acrylic to 17,000 for VAE) demonstrates the large effect that binder can have on paint performance. Very little differentiation can be seen at the highest PVC using this scale. Replotting the data on a logarithmic scale (*Figure* 2) shows an interesting effect that occurs at higher PVCs—the rank ordering of the scrub performance changes dramatically. Some of the paints with the lowest scrub performance at 25 PVC are among the highest at 70 PVC. Differences in the critical PVC due to particle size and other factors may help to explain this effect. Considering that many of the formulations in the EU are at higher than 70 PVC, it is understandable that

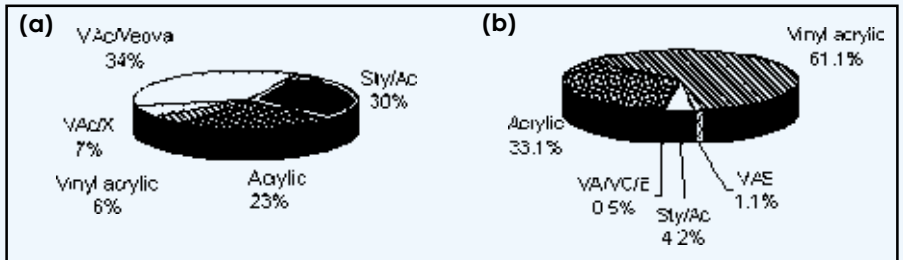

Figure 3—Charts of relative amounts of latex types used in architectural coatings in (a) EU and (b) U.S.[7]

the choice of resin to be used will be different than that in the U.S.

Substrates in Europe are also quite different from those typically used in the United States. Construction methods in the U.S. overwhelmingly favor the use of paper-faced drywall. The majority of substrates in the EU are inorganic, including brick, concrete, lime, or gypsum. This brings additional requirements such as alkaline resistance, and relaxes others—for example, touchup is not important. National standards within the EU vary widely—DIN, AFNOR, VERITAS, BS, GOST, etc. *Figure* 3 shows the relative amounts of different resins used in architectural coatings in the EU versus in the U.S. It can be seen that vinyl acetate-containing resins dominate in both regions; however, the makeup of this segment is quite different between the two regions. The VAc resins in the EU are mainly VAc/Veova resins, accounting for 34% of the overall market. Vinyl acrylics dominate the U.S. market with 61% of the overall water-based architectural market. Significantly more styrene acrylic resin is used in the EU, while the amounts of acrylic are roughly comparable.[7]

While the above data treats the EU as a whole, there are wide variations from country to country within the EU in a number of factors. The prevalence of contractors versus do-it-yourself painters is one. Estimates range from a low of 30% DIY in Greece to a high of 70% in Sweden and Finland.[9] The fraction of water-based versus solvent-based paints used also varies (*Figure* 4). While the overall fraction is 70% water-based, it varies from a low of 40% in France to a high of over 90% in Germany. The average in the U.S. is 80%.[8]

REGULATIONS

Europe

There is a wide disparity in the status of government regulation of VOC use in architectural paints, as shown in *Table* 1. Different definitions of VOC are used, as well as different conventions for calculating it (ppm vs. g/L, with or without water included). Life cycle analysis is a tool finding increasing use as a way to standardize decisions about regulations and to consider the total environmental impact of a coating including frequency of repainting and other factors.

An EU-wide VOC proposal is being considered. It was first proposed by

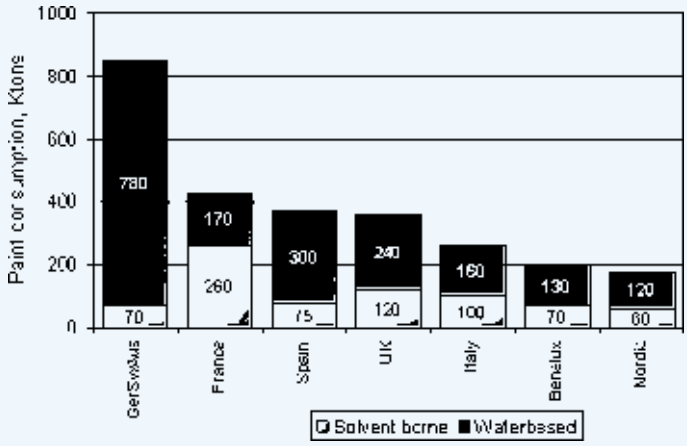

Figure 4—Water-based and solventborne coatings volumes in the EU.[10]

Table 1—Definitions of VOC for Various Regions[11]

Country / Region	Definition
USA/EPA	Any organic compound that participates in atmospheric photochemical reactions except those designated by the EPA as having negligible photochemical reactivity
EU/Ecolabel	Any organic compound with a boiling point less than or equal to 250°C at normal conditions for pressure
EU Solvents Directive	Any organic compound having at 293.15K a vapor pressure of 0.01 kPa or more, or having a corresponding volatility under the particular conditions of use
Geneva Protocol	All organic compounds of anthropogenic nature other than methane that are capable of producing photochemical oxidants by reaction with nitrogen oxides in the presence of sunlight
Australian Paint Approval Scheme	Organic compounds with a vapor pressure of more than 0.01 mm Hg at 21°C, with a boiling point of less than 250°C

CEPE (European Council of the Paint, Printing Ink and Artists' Colours Industry) in 1996, and recently adopted with some revisions in the Netherlands.

Countries in the Nordic region legislated lower VOC levels in paints used by professional painters due to health concerns. Denmark led this movement with legislation effective in 1982, with VOC labeling introduced as early as 1972.[9] Sweden followed in 1987. The Netherlands recently joined this group with restrictions on paints for use by professional painters. Maximum VOC content for interior paints is 75 g/L (including water) effective 1/1/2000. Paints for do-it-yourself (DIY) painters are not regulated.

Germany has no VOC legislation yet enacted, but it is under consideration. The largest impact seems to be from a national ecolabel called Blue Angel created in 1977 that requires very low VOC levels (<700 ppm). A large fraction of the decorative paint used in Germany is water-based, driven by consumer demand.

Several other factors besides direct government regulation have influenced the European market toward lower VOC paints. These include EU-wide voluntary labeling programs (similar to the Blue Angel label previously described) and retailer labeling. The Ecolabel program was launched in 1996. Besides establishing a maximal VOC level for each of several classes of paints, it also requires performance standards and pollution restrictions by the pigment manufacturer whose pigments are used in the paints. In Great Britain, the retail chain B&Q has made a tremendous impact on the paint market with mandatory VOC labeling for the paints it carries.

United States

Regulations restricting the use of VOCs in coatings in the U.S. began in 1966 with Rule 66, which was enacted to control organic solvent emissions in the Los Angeles area. Many regional standards have been set since then, with some of the most influential being the California Air Resources Board (CARB). The Los Angeles area regulated by the South Coast Air Quality Management Division (SCAQMD) is among the most restrictive. Tiered emission limits are in place with reductions scheduled in 2002 and 2006.

No national standards were in existence until the National Architectural and Industrial Maintenance paints and coatings rule (AIM) took effect on September 13, 1999. Since most paint companies sold paint in regions where restrictions were in force, the national standards had relatively little effect; the EPA estimated that less than 0.1% of industry volume did not meet the VOC limits and would be discontinued.[12] Regions are still allowed to enact standards more stringent than those outlined by AIM.

Tighter regulations are expected soon for the Northeast as well. The Ozone Transport Commission (OTC), which has authority to recommend VOC regulations for Maryland, Delaware, Virginia, and the remaining Northeast, recommended in March 2001 a model rule for VOC restrictions on coatings similar to those already enacted by CARB.

A comparison of VOC levels for some of the regulations and voluntary labeling schemes is shown in *Table* 2. Quite a difference is seen between relatively high AIM levels and extremely low levels required for Blue Angel or B&Q minimal labels at virtually zero. The EU-wide CEPE proposed limits are most similar to the South Coast limits.

FORMULATING LOW VOC PAINTS

The most obvious source of VOCs in architectural paints is coalescing solvent. There are many other sources that may need to be considered, depending on the desired formulation level. In order to produce paints considered zero VOC, the list is

Table 2—VOC Levels in g/L of Various Regulations and Labeling Schemes

Region	Effective Year	Interior Flat/Matte WB	Interior Nonflat WB	Exterior Flat WB	High Gloss
AIM	1999	250	380	250	380
CARB	2003 rec	100	150	100	250
SCAQMD	2001/2008	100/50	150 (2002) 50 (2006)	100/50	—
CEPE	pending	55/30	150/100	60/40	—
Ecolabel	1996	30	200, 250 if high hiding	—	—
NF Environment	1992	125	250	—	—
Blue Angel	1977	~1	—	—	—
B&Q minimal VOC level, GB	—	4	—	—	—

daunting: coalescing solvent, glycol, additives including surfactants and rheology modifiers, buffers, etc.

While it is possible to choose raw materials and formulations to give good performance in many areas, some performance areas are quite challenging. Low T_g resins allow good film formation without coalescing solvent or at reduced levels. Solvents such as Texanol (Eastman) or Butyl Carbitol (Union Carbide Corp.) can be replaced with plasticizers or with alternative solvents which contribute nothing or only a fraction of their weight to the VOC content. Many additives are now being offered in higher active or even water-based versions.

Freeze thaw resistance is extremely challenging to maintain at low VOC levels. Formulating at low or no glycol impacts open time and wet edge properties. The issue of low odor versus low VOC is not clear-cut, as different odors become apparent when solvents are removed.

One of the most significant challenges remaining is formulating high gloss coatings at low VOC. High gloss paints normally require hard resins in order to give acceptable block resistance. This high T_g requires high solvent levels in order to get good film formation.

CONCLUSIONS

History has shown that trying to predict the future is a thankless task. Nevertheless, a few comments are in order about current trends and their projection into the future for the coatings industry.

The number of paint companies in the U.S. has decreased steadily in recent years due to acquisition or consolidation of regional companies. This trend is expected to continue as pressure from large consumer outlets increases. Some consolidation of paint lines within a single supplier might be expected. Rising energy costs greatly impact transportation costs for paint products, and a shift to producing all products in multiple locations rather than a portion of the product line in each plant and shipping to different regions to reduce these transportation costs might be seen.

Conversely, an opposite effect might be seen with new technology. Coatings Management Systems has developed a system in which four different liquid components can be combined for up to 450 different SKUs of paints.[13] This would allow a consumer to specify particular properties and have the paint made to order—a large step up from simply mixing colors.

From the standpoint of resin development, it seems likely that the number of new monomers introduced will be relatively small. Advances in paint resin technology will likely be more in line with recent changes in the polyethylene market—enhanced properties from controlled morphology or process changes.

The architectural coatings market will respond to the latest challenge—legislation reducing the allowable level of VOCs in their products—with the same response as in the past. Paint companies will identify new or existing technologies that will allow them to offer a range of products to meet or exceed their customers' needs.

References

(1) Bullett, T.R., "Paint: A Changing Spectrum," *Rev. Prog. Coloration*, Vol. 14, pp. 78-83 (1984).
(2) World wide web, National Paint and Coatings Association website www.paint.org/ind_info/history.htm.
(3) Brewer, G.E.F., "History of Painting: 75 Years," *Plating and Surface Finishing*, June, pp. 57-60 (1984).
(4) Pike, A., "Nineteenth and Twentieth Century Marker Materials in Architectural Paint," English Heritage, London, pp. 56 (1994).
(5) Boxall, J., "A History of Paint Technology, Part II: Mid-19th Century to 20th Century," *Paintindia*, July, p. 6–12 (1982).
(6) Stevens, V.L., "History of Styrene Copolymer Coatings in Organic Coatings; Their Origin and Development," in *Organic Coatings: Their Origin and Development*, Seymour, R.B. and Mark, H.F. (Eds.), Elsevier Science Publishing Co., pp. 323–340 (1990).
(7) Anonymous, "Coatings VI, A Multiple Client Study," Skeist Inc., Whippany, NJ.
(8) Mesbah, B. et al., *Paint and Coatings 2000: Review and Forecast*, 2nd edition, National Paint and Coatings Association Management Information, Kline and Company, New York, 1998.
(9) Anonymous, "Decopaint—Study on the Potential for Reducing Emissions of Volatile Organic Compounds (VOC) Due to the Use of Decorative Paints and Varnishes for Professional and Non-professional Use," Final Report, EC DG Environment Tender E1/ETU/980084, pp. 316 (2000).
(10) pra COMET, Vol. 2/98, p. 79ff (1998).
(11) Kershaw, Y., "VOC Legislation on the Threshold of Change," *Eur. Coat J.*, No. 4, pp. 230-235 (1998).
(12) Walker, J.H, "Coming Clean: How Pending Environmental Regulations Will Affect Paint and Coatings Formulators," *Mod. Paint Coat.*, April, pp. 16-41 (2000).
(13) Anonymous, "Will This Be the Future of Paint?," *The Paint Dealer*, May, p. 26-27 (2001).

Appendix A—Formulations for PVC Ladder Study

PVC	25	40	57.25	70.3
Vol solids	30.9	30.94	30.9	31.05
lb/gal	9.959	10.718	11.553	12.197
Ingredient				
Natrosol 250HR (Aqualon)	2	2	2	2
Water	98	98	98	98
AMP95 (ANGUS)	3	3	3	3
Ethylene Glycol	20	20	20	20
Texanol (Eastman)	16.07	12.1	8	5.29
Igepal CO-610 (Rhone-Poulenc)	3	3	3	3
Drew L-475 (Drew Industrial Div.)	2	2	2	2
Tamol 850 (Rohm and Haas)	5	5	5	5
TiPure R-901 (DuPont)	100	151	200	230
Satintone #1 (Engelhard)	25	37.8	50	57.5
Snowflake (ECC International)	25	37.8	50	57.5
Al-Sil-Ate NC	37.5	56.7	75	90
Goldbond R	37.5	56.7	75	90
NuoSept 95 (Hüls)	1	1	1	1
Water	55	55	55	55
Natrosol 250HR (Aqualon)	3.5	3.5	3.5	3.5
Water	171.5	171.5	171.5	171.5
Drew L475 (Drew Industrial Div.)	2	2	2	2
Water	75	91.9	104	109.7
Latex (55% solids)	462	348	230	152
Total	1144.07	1158	1158	1157.99