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Plastics Additives
and Modifiers
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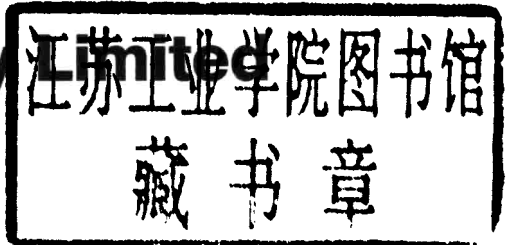
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Polymers & Additives Trends in the 21st Century

Dieter Morath

Great Lakes Chemical Corporation, Basel, Switzerland

First of all let me say it is a pleasure to be here to share a few of my views on the trends of Polymers & Additives in the 21st Century. I started to say the new millenium, but if you're like me you've grown tired of a worn out phrase, so from here forward I'll use 21st century. I wanted to begin with a story about a teacher who asked a student to sum up Socrate's life in four lines.

- Socrates lived long ago
- He was very intelligent
- Socrates gave long speeches
- His friends poisoned him!

With that in mind I'd like to **briefly** talk about five trends I see in the polymers & additives market in the 21st Century.

1. GROWTH

Demand for plastics today is very healthy, and we at Great Lakes think that the industry is expected to continue to experience growth rates at higher than projected GDP rates. Today, the total production for global polymers is greater than 150 billion tons, and consumes \$7.2 billion worth of chemical property extenders and other additives. While global GDP (for all industries) is projected to be approximately 3.5% through 2005, the polymers industry is forecasted to have a robust compounded annual growth rate of 4-5%. A number of segments, particularly polyolefins and engineering thermoplastics are projected to grow at rates greater than 5%. We believe the additives market will continue to grow at rates **faster** than the polymers markets, as polymer and resin producers seek to modify their products to bring lower costs, and additional benefits to their customers. The need for plastics to meet tougher standards will also facilitate this growth. An example of this is in the flame-retardants industry, where tougher furniture flammability standards are being discussed in many states. New legislation could force polyurethane foam producers to modify their products to meet these new tougher standards, making their products safer for consumers.

In Europe, tougher flammability legislation for business machines and television sets are being discussed. Polymers once thought to be limited to low end applications are challenging traditional high end polymers, due to polymer modifiers, additives, and resin modification. Recyclability will force plastics and resin producers to modify their products to meet tougher legislation and regulatory demands. In short, we believe the polymers industry will continue to experience strong growth rates and the additives market will grow even faster. We should be excited about this as additive suppliers!

Globalization

As much as in any industry, the polymers industry is truly global. The polymer industry no longer segregates itself into three geographic regions. The major players in the market today are making their presence known globally. Three trends have emerged:

a. Developing regions will grow tremendously and developed regions growth will slow over the next five years.

Asian polymer demand, particularly polyolefins, will grow significantly and will exceed the US demand by 2005. The demand for additives and modifiers in this region will follow. Polymer producers who want to compete long term and maintain a leadership position will invest in areas such as China, Southeast Asia, the Middle East, and Latin America. Regional trends and developments will have impact on global producers.

b. Demand for additives will become more standardized across regions.

Global consolidation by resin producers and plastics companies will create demands for additives that have the same properties and characteristics across the globe. Global plastics standards, driven by end use industries (OEMS) will force consistency in products. A recent example of this is the globalization of monitor standards. Greater than 80% of monitors produced are produced in Asia. Because of this, they also set the specifications for materials which are used all over the World. The European ecolabels are also influencing product choice outside of Europe because of the producers needs to service global markets. Another excellent example of this is the automotive industry. A Japanese car maker will specify a particular polymer grade for a component and he will expect the component made from that grade, containing exactly the same additive package, to be available at his plant in the U.S. In some cases this has even led to Japanese owned compounders starting up in the U.S., and sourcing identical additives to meet these needs.

c. Additive companies will have to be global in order to compete.

Consolidation, commoditization, cost demands, and service requirements will all push additive producers towards focusing on having a global presence. "Think global, act local" has already become the mantra. Those companies who have local production enjoy the advantage of speed, service, local production "psyche", and cost advantages (such as the avoidance of freight and duties) and can work in local currencies where beneficial. Taking advantage of lower capital, and labor costs will help to insure that additive producers maintain a cost competitive position in the future.

Summary Story

The story goes that there was a vacuum cleaner salesman who called on a farm wife in Mexico. He dumped a disgusting pile of dirt on her floor and said, "if this machine doesn't get your carpet clean, I'll eat it." the woman turned toward the kitchen, to which the salesman asked, "where are you going?" "to get the salt", she replied. "our house isn't wired for electricity!" The successful additives company will understand the need for globalization, will invest in the developing regions, but must face the challenges that go with it!

3. CONSOLIDATION

Global consolidation, both in the polymers industry and the additives industries, have been a trend for several years. The competition for growth in the developing regions will continue to push consolidation for several reasons.

- Achieve economies of scale on a world class basis
- Expand product line and geographic scope
- New technologies
- Lower costs through rationalization and raw material leverage
- Global information technology capability

In the polyolefin industry, especially, there have been a number of mergers creating larger more dominant suppliers. The top ten polyolefin producers will have close to 50% market share in 2000, as opposed to 40% in 1999. In the polystyrene industry, Nova has recently acquired both Huntsman and Shell. In Japan, the number of polystyrene producers have gone from 10 to 4 in recent years. The engineering polymers industry has had a number of strategic alliance activities focusing on synergism created by company strengths, and focused on targeted markets.

Consolidation by the polymer producers will have a dramatic effect on the additives producers as well. Already, there have been a number of strategic mergers and acquisitions, joint ventures, and partnerships formed in the additives industry, as additive producers seek to broaden their product portfolios, and provide solution selling versus product selling.

- GLCC/Enichem/Anzon/FMC
- Ciba/ Mallinrodt/ Baerlocher/ Prochemica
- Albemarle / Ferro (proposed)/ US borax
- CK Witco/ Uniroyal
- Rohm & Haas/ Morton Intl.

The large amount of merger and acquisition activity in the polymer/ plastics industries will force additive producers to reconsider their strategies both vertically and horizontally.

The challenges are as follows:

- Cost competitiveness (additives suppliers must respond to the leverage created by larger customers, who prefer fewer suppliers)
- Broad based solutions- customers want an additives company that can bring a range of new ideas/ new solutions and not just products

- Global service-ability to meet global demands, such as R&D, and technical service, not to mention delivery, on a global scale
- Consistency of supply - customers want the same product specifications globally
- Ability to adjust to new standards, regulations, and environmental concerns - fast!

To summarize - the needs of the polymer producers and the plastics industry will force consolidation in the additives industry. The successful additives company must drive quickly towards this consolidation in order to remain competitive!

4. E-BUSINESS

I've already mentioned that to be successful, additives companies must be global, and they must address their strategy for consolidation. I believe **E-business** will also be a pre-requisite if not now, in the very near future. E-business is more than electronic commerce - the buying and selling of products electronically. It's about strategy. As customers grow, they will demand strategic relationships through business to business activities.

A. why e-business?

Additives suppliers must evaluate the traditional business design where in house competencies were the basis for all decisions that were made throughout the value chain. Customer segmentation was an afterthought to those core competencies. Today, the e-business value chain model will force companies to evaluate the needs of their customers first, and position themselves through channeling, solutions, and infrastructure in order to meet those needs. If successful, additive companies can find value in differentiating themselves from their competition.

B. e-business challenges today:

With the rush to market the real challenge is whether E-business can deliver value to companies. New business channels mean new opportunities! There is little doubt that companies today are driving in this direction.

- Global markets fragmented by regional differences.
- Rush to market.
- Partnering with service providers.
- Challenge to traditional channels: direct, regional, distribution, agents.
- Limitations: focus on commodity, non-global, fragmented, information overload.
- Revolution vs. evolution: value yet to be derived?
- ERP to ERP.

C. finally- what do customers want?

While value creation will be a challenge, there is little doubt as to what customers are looking for through E-business:

- Speed
- Ease of use
- Global access

- Information
- Cost-value!

A successful E-business strategy must focus (at its core) on the customer, and in meeting their E-business requirements!

5. OTHER TRENDS

As a final thought I would like to highlight several other trends that will have importance to polymers & additives.

- A. **Interpolymer Competition** - Competition between resins will be more fierce as OEMs push for differing properties, and drive out cost. This chart shows an example of the interpolymer competition in the electronics market. Through intrinsic modification, alloying, or additive use, lower valued polymers can then migrate to higher end use applications.
- B. **Cost Performance** - will continue to play a major role in determining what polymers are used. The electronic and automotive industries are examples of extreme cost pressure. Additives, modifiers, and catalysts will play important roles in lowering the cost of finished products, while driving higher performance. Developing niche applications or added benefits will be the key to increased polymer additive profits!
- C. **Environmental/Regulatory Pressures** - the push towards more environmentally and exposure friendly products and product forms will play an important role in the future of the additives products. Pellets (and other

product forms) are replacing powders to eliminate dust concerns. Over the last several years voluntary ecolabel initiatives have prompted companies to consider alternatives to the traditional additives used. Recycle and biodegradable requirements have resin producers looking at new products and additives that meet these criteria. As polymer and plastics companies struggle to meet the new environmental and regulatory pressures there will be tremendous opportunity for additives producers to differentiate themselves with solutions that meet these new demands.

- D. **Miniaturization**- physically, plastics are required to be used in smaller parts. This forces changes in polymers used or increases the need for additives in existing polymers to maintain physical integrity and give better flow properties.

CONCLUSION

Growth, globalization, consolidation, E-business, and additive changes are all trends we are facing and serve as opportunity and challenge for us all as a polymer additives industry. In closing, I'd like to say that God gave us two ears, but only one mouth. Some people say that's because he wanted us to spend twice as much time listening as talking. Others claim its because he knew that listening was twice as hard.

Thank-you for listening today! I hope you have a fruitful conference.

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Flexible Vinyl Medical Products: Discussion about the Extraction Characteristics of Various Plasticizers

Richard C. Adams

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ABSTRACT

The use of plasticized polyvinyl chloride (PVC) for toys and medical devices has been under attack from various environmental and health care activist groups. Their concerns are related to, that under certain conditions small amounts of the plasticizer may leave the flexible PVC compound (an act referred to as leaching, migrating, or extraction). This extracted plasticizer can then enter the human body and then, allegedly, cause damage ranging from cancer to hormone disruption. The plasticizer under the most scrutiny is di(2-ethylhexyl) phthalate, commonly known as DEHP or DOP. DEHP is the largest volume plasticizer in use worldwide and the most widely used plasticizer for PVC medical devices. This paper will not address the relative toxicity of plasticizers but will look at the various mechanisms under which plasticizers leave the flexible PVC medical devices. To accomplish this we will review available information, from Hatco Corp., Morflex, Inc. and BP Amoco, on the migration and extraction characteristics of various plasticizers, including DEHP, TOTM, Citrates and Adipates. Discussing potential selection criteria based on plasticizer permanence.

EXPERIMENTAL

All of the extraction data reported here came from published sources^{1,2,3}. The test methods while similar are not as controlled as if they had been completed in one laboratory in a similar time frame and with identical extraction media. In addition the variations in sample thickness must be remembered as the thicker samples will have lower percentage weight loss in a particular media for a given time. Data was selected from published information from Hatco Chemicals, Morflex Inc. and BP Amoco Chemicals. In the effort to compare the extraction resistance of plasticizers evaluated in different laboratories by slightly different techniques, we compared the relative extraction resistance to plasticizers that each study had in common. Such as, dioctylphthalate (DOP) and dioctyladipate (DOA) were used as reference points assuming that their extraction characteristics are relatively constant time to time and batch to batch.

Hatco¹ choose to adjust the plasticizer levels in their study to create molded compounds that were at a constant or a standard 100% modulus value. The Hatco compounding procedure was that the ingredients were mixed well by spatula and then charged to a 2 roll, 15 cm by 33 cm mill heated to between 140°-177°C, depending on the compound, for 5 minutes from the point that it fluxed. The milled sheet

was compression molded to its final thickness at 177°C for 5 minutes at 6,900 kPa. Samples were die cut and placed in a CT Room at 23°C and 50% relative humidity for a minimum of 40 hours prior to testing. For Extraction testing three die cut samples, 50.8 mm in diameter by 0.5 mm thick were accurately weighed and suspended in the extraction media. The samples were held at temperature for the time period shown in the **Table 1**. After extraction, the specimens are dried, aged, and reweighed. The weight loss was then computed as percentage of the original weight of the sample.

Morflex² held the amount of plasticizer in the compound constant, for all of the plasticizers, and allowed the hardness and modulus to vary. The ingredients were mixed and then placed on a 2-roll mill for 5-10 minutes at 163°-171°C. The milled stock was compression molded for 3 minutes at 171°-182°C at 220 MPa. For extraction 1.0 mm sheet was first conditioned for 48 hours at 24°C before exposed to extraction. The conditions are listed in **Table 2** but one difference from other data reported here is that Morflex choose to report, not percentage weight lost but, percentage plasticizer lost.

In the BP Amoco procedure, as with the Morflex procedure, the level of plasticizer was held constant. The ingredients were mixed in a planetary mixer and then placed on a 2-roll mill for 10 minutes at 163°-166°C. This milled sheet was then compression molded to the desired thickness (1 mm) for 8 minutes at 174°C and 6,900 kPa. From the molded sheet 50.8 mm diameter disks were cut. These sample coupons were then exposed to the conditions listed in **Table 3**, and then dried before weighing.

DISCUSSION

In the literature⁴ several factors are discussed that influence the rate of extraction for a plasticizer to a particular media. The surface area of the test specimen and the diffusion rate of the plasticizer through PVC control the extraction rate of a plasticizer. The efficiency at which a given test media can remove plasticizer from the surface of the test specimen is the first level of control on the rate of plasticizer extraction/migration. When the extraction media is one in which the plasticizer is not particularly soluble and the capacity of the media to hold the plasticizer is low. Examples of this are water and saline solution. Then the efficiency of plasticizer removal from the surface will be poor hence the rate of plasticizer loss from flexible PVC will be slow. When the media is more efficient at removing plasticizer from the surface of the plastic and holding it in solution, as is the case with soapy water and natural body fluids such as blood,

diffusion of the plasticizer through PVC becomes the controlling factor determining rate of plasticizer loss to the media. The size and the shape of the plasticizer molecule control the diffusion rate, where the larger and bulkier the plasticizer molecule, the slower the diffusion rate. It also has been found that if the plasticizer was produced from branched alcohols that they would diffuse at lower rates than plasticizers based on linear alcohols. Considering this, if one wanted to reduce the diffusion rates, one would choose a bulky plasticizer molecule that was manufactured with branched alcohols. In addition to the previously mentioned factors influencing the extraction resistance of a plasticizer to a given test media, the ability of the test media to permeate into the flexible PVC mix can be an additional factor that can influence the diffusion rates of the plasticizer and the plasticizer's compatibility.

The presence of even small amounts of materials that can hold large amounts of plasticizer in a liquid that is otherwise a poor extractant, can completely change the rate and extent of extraction. The most common example of this is the presence of micelles formed by soap and other surfactants in water. Another common example is that of natural body fluids, such as blood, which has much the same ability. M. S. Jacobson reported⁵ (1980) that as the concentration of blood plasma protein increases the amount of plasticizer extracted into the extraction media increases. This was the result of his extraction studies with various dilutions of blood plasma and saline solution up to 100% blood plasma.

The selected plasticizers have been evaluated in a number of different extraction media, but for the purposes of this talk we will focus on water, soapy water and mineral oil to determine the relative extraction resistance. We have included hexane extraction for reference purposes but do not believe that it is representative to any medical exposure media.

From the Hatco's literature we have chosen 4 plasticizers to compare; dioctylphthalate (DOP), trioctyltrimellitate (TOTM), dioctyladipate (DOA) and a polymeric Hatcol 640 that has a theoretical molecular weight of 2500. From the Morflex literature we have chosen 5 plasticizers. Again we will look at DOP and DOA but in addition for comparison

Morflex's three citrate offerings, acetyltri-n-butyl citrate (Citroflex™ A-4), acetyltri-n-hexyl citrate (Citroflex™ A-6), and n-butyltri-n-hexyl citrate (Citroflex™ B-6), will be compared. From the BP Amoco literature we will look at DOP, TOTM and two polymeric adipate type plasticizers of molecular weights 3300 and 1800. When comparing Hatco's studies to Morflex's the relative extractabilities of the common plasticizers, DOP and DOA, were used. Whereas when comparing the Hatco and Morflex's studies to the BP Amoco extraction study the relative extractability of DOP was used.

Dioctylphthalate is the main plasticizer used for medical applications, but citrates are being touted as a lower toxicity plasticizer. To this comparison we have added trimellitate and polymeric plasticizer to demonstrate a range of extractabilities.

Water is by far the least aggressive media reviewed here and is also likely not to be as aggressive as blood plasma but is likely to be similar in aggressiveness to a standard saline solution. In this media TOTM was the least extracted followed by DOP, see **Table 1** and **2**. It would appear that DOA, H-640 and the citrate plasticizers fall into the same range of extractability. By comparing The relative extractability of DOP and DOA from the Hatco and Morflex literature a relative placement can be made for the other plasticizers.

Soapy water is a far more aggressive media than water. The main reason is that the soap micelles are more efficient at removing any plasticizer at the surface of the test specimen and isolating the plasticizer so that it can not migrate back into the PVC. The proteins in plasma are reported to have similar effect. Again the trioctyltrimellitate is the least extractable of the plasticizers followed by all the polymeric plasticizers and n-butyltri-n-hexyl citrate.

The polymeric plasticizers are best in mineral oil followed by trioctyltrimellitate. Acetyltri-n-butyl citrate performs better than dioctylphthalate in mineral oil.

Table 1. Performance of Plasticizers Compounded to a Standard Modulus (0.5 mm Film Thickness)

	DOP	TOTM	DOA	H-640
Concentration, phr	54	56	42	62
Hardness, Shore A	80	84	81	84
100% Modulus, MPa	10.3	10.5	10.3	10.4
Tensile Strength, MPa	18.3	18.6	17.6	16.8
Elongation, %	330	370	380	320
Brittleness Temperature, TB, °C	-27	-22	-45	-15
Weight Loss by Extraction, %				
Water (24 hrs. @ 50°C)	0.2	0.13	0.40	0.52
1% Soapy Water (24 hrs. @ 50°C)	5.3	0.12	16.5	4.6
Mineral Oil (24 hrs. @ 50°C)	11.6	7.1	18.1	1.9
Hexane (1 hr. @ 25°C)	22.0	23.8	32.0	1.7
<i>Technical Information Bullet, Hatco Chemical</i>				

Table 2. Performance of Plasticizers Compounded to a Standard Modulus (1.0 mm Film Thickness)

	DEHP (DOP)	DEHA (DOA)	ATBC	ATHC	BTHC
Concentration, phr	50	50	50	50	50
Hardness, Shore A	79	78	78	81	81
100% Modulus, MPa	9.4	7.5	9.3	10.9	9.4
Tensile Strength, MPa	18.9	12.4	19.7	20.5	20.2
Elongation, %	395	414	400	390	427
Brittle Point, °C	-24.5	-56.5	-18.5	-26.0	-33.5
% Plasticizer Loss by Extraction, %					
Water (tap), (24 hrs. @ 60°C)	0.7	1.5	1.2	1.9	1.7
1% Soapy Water (24 hrs. @ 60°C)	2.7	11.0	9.5	5.4	2.2
Mineral Oil #3, (24 hrs. @ 60°C)	11.3	34.7	10.9	13.8	15.7
Technical Bulletins 101 and 103, Morflex, Inc.					
Formulation	Parts by Weight				
PVC	100				
Plasticizer	50				
Calcium/Zinc Stabilizer	2.5				
Stearic Acid	0.25				

CONCLUSIONS

Based on extraction studies, if the desired outcome was to reduce the amounts of plasticizer that is being extracted from a flexible PVC Medical device then trimellitates would be a good choice for a variety of media. While citrates are offered as a non-toxic alternative plasticizer they are extracted at a rate that would appear to be higher than that of TOTM and most often more extractable than DOP. As with any decision on a material choice there are often many issues to be considered beyond that of extractability alone. In this talk we have chosen to look at extraction resistance only and this may not be the main criteria for all applications.

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**Table 3. Comparison of Trimellitate, Phthalate and Polymeric Plasticizers in a General Purpose Compound¹
(1.0 mm Sheet)**

	TOTM	DOP	TOTM	Adipate MW 3300	Adipate MW 1800
Concentration, phr	50	50	62	62	62
Hardness, Shore A, 10 sec.	93	86	86	86	86
100% Modulus, ASTM D412, MPa	13.5	10.3	9.4	11.0	10.3
Tensile Strength, ASTM D412, MPa	19.7	17.5	17.7	19.3	18.9
Elongation, ASTM D412, %	330	350	390	380	400
Brittleness Temperature, ASTM D746, °C	-26	-27	-37	-15	-16
Carbon Volatility, ASTM D1203					
% wt. Loss after 24 hrs. @ 90 °C	0.4	1.7	0.3	0.6	0.6
% wt. Loss after 48 hrs. @ 90 °C	0.4	3.0	0.3	0.6	0.7
Soapy Water Extraction, ASTM D1239					
% wt. Loss after 48 hrs. @ 90 °C	0.1	3.2	0.1	4.0	6.3
% wt. Loss after 72 hrs. @ 90 °C	0.3	7.6	0.3	5.6	7.9
Mineral Oil Extraction, ASTM D1239					
% wt. Loss after 24 hrs. @ 70 °C	2.5	3.2	3.5	1.5	2.0
Hexane Extraction, ASTM D1239					
% wt. Change after 24 hrs. @ 23 °C	-12	-11	-18	+2	+2
Humidity Compatibility					
% wt. Loss after 7 days @ 70 °C	0.1	0.3	0.1	0.3	0.3
% wt. Loss after 7 days @ 90 °C	0.2	0.8	0.2	0.4	0.4
Bulletin TM-46d, BP Amoco Chemical Company					
Formulation	Parts by Weight				
PVC	100				
Plasticizer	50				
Barium Cadmium Stabilizer	2.0				
Zinc Stabilizer	0.5				
Stearic Acid	0.5				

Benzoate Plasticizer for Reducing Plastisol Viscosity and Fusion Temperature

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ABSTRACT

Viscosity control of plastisols is a major consideration in the formulation of a vinyl product produced by methods such as spread or reverse roll coating. The application conditions often dictate the addition of a diluent in the formulation to lower the rheology of the plastisol for successful processing. A benzoate plasticizer has been introduced that has the capability of lowering plastisol viscosity while also performing as a highly solvating plasticizer. This unique combination is illustrated in both phthalate and benzoate containing plastisols and the properties of both the plastisol and final sheet are presented.

INTRODUCTION

General-purpose plasticizers used in flexible vinyl products often require viscosity reduction for efficient plastisol processing in continuous coating applications. This usually requires using a viscosity reducing diluent in the formulation. There are a number of specialty plasticizers and diluents that can be used to reduce and control viscosity.^{1, 2} Often the specialty plasticizers or viscosity reducing diluents are poor PVC solvators, inefficient plasticizers, result in poorer vinyl sheet physical properties, and often increase the gelation and fusion temperatures of the plastisol. In some instances, the cost of the specialty plasticizers also reduces their potential use.

Plastisol producers in various regions of the world have been looking for alternative viscosity reducing diluents with better plastisol and sheet properties compared to existing products. Typical desired improvements are reduced volatility, improved physical properties of product, and reduced environmental concerns. In an effort to respond to various market needs, 2-ethylhexyl benzoate was identified as a potential cost effective, viscosity reducing, highly solvating plasticizer. The purpose of this paper is to show that 2-ethylhexyl benzoate is a new, effective plasticizer for reducing viscosity, improving processing latitude and improving product quality compared to a commonly used diluent.

EXPERIMENTAL

Plastisols were prepared in a high shear mixer at 2000-2500 rpm for 10 minutes and degassed for 15 minutes while stirring at 200 rpm with vacuum maintained at less than 10 torr.

Low shear viscosity measurements were conducted on a Brookfield RVT viscometer at 25°C. Rheological measurements were conducted on a TA Instruments CSL² 100 rheometer at 25°C with a 2 cm. flat plate spindle. The plastisol gelation temperature was generated on a TA Instruments CSL² 100 rheometer, ramped at 0.75°C/minute, and measured in the oscillation mode with a 2 cm. flat plate spindle. The gelation temperature was measured at a G' value of 500 Pa.

Fused vinyl sheet samples were prepared in a Werner Mathis oven on release paper with a drawdown thickness of 0.25 mm and 1 mm. The oven temperature was 200°C and the oven residence time was 2 minutes.

Volatile loss during fusion (fusion process volatility) was determined by gelling the plastisols (1 mm drawdown) in a Mathis oven at 160°C for 18 seconds, cutting 7.62 cm samples, equilibrating and weighing them, fusing them in a Mathis oven at 200°C for 120 seconds, equilibrating the samples, and reweighing them to determine weight loss.

Sheet volatility with activated carbon was determined by using ASTM D1203. Low temperature flexibility was measured by using ASTM D1043, and tensile properties were determined by using ASTM D-638. Shore A hardness was measured by ASTM D2240, and extraction testing was done with ASTM D-1239.

RESULTS AND DISCUSSION

2-Ethylhexyl benzoate was identified as a viable candidate plasticizer by screening a number of key properties. **Table 1** compares some of these key properties, namely plasticizer viscosity, TGA weight loss, and plastisol gelation temperature, for four viscosity-reducing plasticizers. The Ap/Po ratio³ for 2-ethylhexyl benzoate is 8. Combination of this datum with the branched nature of 2-ethylhexanol suggests that there is a reasonable possibility of low PVC interaction with this plasticizer. This basic information supports the idea that 2-ethylhexyl benzoate has potential as a commercially viable viscosity reducing plasticizer for PVC plastisols that can also provide reduced volatility, lower gel temperature, and be a cost effective diluent.

A series of PVC formulations containing DOP as the primary plasticizer and 2-ethylhexyl benzoate or 2,4,4-trimethylpentan-1,3-diyl diisobutyrate as the viscosity reducing plasticizer are given in **Table 2**. **Table 3** contains some of the plastisol and sheet properties of these formulations. In addition, a series of PVC formulations containing DINP as

Table 1. Plasticizer Properties

Plasticizer	Viscosity @ 0°C (Pa.s)	TGA, 50% Weight Loss Temperature 10°C/min ramp	Plastisol Gelation Temperature (°C)
2-Ethylhexyl benzoate	0.017	197	57
Isodecyl benzoate	0.027	223	67
2,4,4-Trimethylpentan-1,3-diol diisobutyrate	0.017	174	73
Dodecyl benzene	0.024	179	

Table 2. Basic PVC/DOP Plastisol Formulation

Formulation	A	B	C	D	E
PVC (Geon 121A)	100	100	100	100	100
DOP	50	40	40	30	30
2-Ethylhexyl Benzoate		10		20	
2,4,4-Trimethylpentan-1,3-diol diisobutyrate			10		20
ESO	2	2	2	2	2
Ba/Zn Stabilizer	4	4	4	4	4

the primary plasticizer and 2-ethylhexyl benzoate or 2,4,4-trimethylpentan-1,3-diyl diisobutyrate as the viscosity reducing plasticizer are given in **Table 4**. **Table 5** contains some of the plastisol and sheet properties of the DINP formulations.

A third series of formulations made with European resins and plasticizers commonly used in flooring applications are listed in **Table 6**. Plastisol and sheet properties for the flooring-type formulation are presented in **Table 7**.

BASIC PVC FORMULATIONS

Plastisol Properties

Benzoate plasticizers are commonly thought to have high viscosity. However, it is apparent in **Table 3** and **Table 5** that 2-ethylhexyl benzoate is a very effective viscosity reducer. Viscosity reduction is generally lower with 2-ethylhexyl benzoate than for formulations containing 2,4,4-trimethylpentan-1,3-diyl diisobutyrate, a commonly used viscosity reducing additive. Viscosity stability was similar for the DOP or DINP formulations containing either 2-ethylhexyl benzoate or 2,4,4-trimethylpentan-1,3-diyl diisobutyrate.

Benzoates are generally known as highly solvating plasticizers. The gelation temperature was definitely lower for the formulations containing 2-ethylhexyl benzoate. If lower processing temperatures or faster processing speeds are required, 2-ethylhexyl benzoate is one of the few viscosity reducing plasticizers that also significantly lowers the gelation temperature of general purpose plasticizers.

Fused Sheet Properties

Fused sheet properties can be negatively impacted with the use of a viscosity reducer in the formulation. **Table 3** shows that the low temperature flexibility of the DOP based formulation is negatively impacted by the addition of the viscosity reducing plasticizers. The 2-ethylhexyl benzoate

formulations show better low temperature flexibility properties than formulations containing 2,4,4-trimethylpentan-1,3-diyl diisobutyrate. However, the DINP formulation in **Table 5** shows the low temperature flexibility property is improved with the use of 2-ethylhexyl benzoate in the formulation.

The standard mechanical properties in **Tables 3** and **5** shows that 2-ethylhexyl benzoate appears to be a more efficient plasticizer than 2,4,4-trimethylpentan-1,3-diyl diisobutyrate. The Shore A hardness, ultimate elongation, and 100% modulus in **Table 3** and **Table 5** generally show higher plasticizer efficiency results for 2-ethylhexyl benzoate than 2,4,4-trimethylpentan-1,3-diyl diisobutyrate. The DOP and DINP based formulations containing 2-ethylhexyl benzoate have a lower 100% modulus and higher ultimate elongation than the formulations containing 2,4,4-trimethylpentan-1,3-diyl diisobutyrate. The Shore A hardness is very similar for all the formulations, but again the Shore A values are lower (higher plasticizer efficiency) for the formulations containing 2-ethylhexyl benzoate in place of 2,4,4-trimethylpentan-1,3-diyl diisobutyrate. Results listed in **Table 3** and **Table 5** show tensile strength is negatively impacted in both the DOP and DINP formulation results with the addition of either viscosity reducing plasticizer.

There is no significant plasticizer extractability differences observed between the formulations containing either 2-ethylhexyl benzoate or 2,4,4-trimethylpentan-1,3-diyl diisobutyrate in combination with either DOP or DINP in **Tables 3** and **5**.

Volatility properties were pretty much as expected. As the level of the viscosity reducing plasticizer increased, volatile weight loss also increased. The 2-ethylhexyl benzoate formulations in general exhibited a lower volatile weight loss with charcoal than the formulations containing 2,4,4-trimethylpentan-1,3-diyl diisobutyrate.

Table 3. Basic PVC/DOP Plastisol Screen					
Formulation from Table 2	A	B	C	D	E
Brookfield Viscosity @ 20rpm, (Pa.s), 1 day post-mixing					
1 Day	8.0	4.6	4.7	2.9	2.6
Viscosity @ 20 sec.⁻¹ (Pa.s)					
Initial	7.4	3.7	3.8	2.0	1.8
1 Day	9.2	4.5	4.4	2.4	2.2
3 Day	9.8	4.8	4.8	2.7	2.3
Viscosity @ 100 sec.⁻¹ (Pa.s)					
Initial	24.2	6.8	7.3	3.0	2.8
1 Day	36.4	8.7	9.2	3.7	3.5
3 Day	40.4	9.5	9.9	4.1	3.7
Gelation Temperature (°C)					
1 Day	72	69	72	66	72
Mechanical Properties					
Low Temperature Flexibility					
	-28°C	-26°C	-23°C	-25°C	-22°C
Tensile Strength (MPa)					
	19.7	19.0	18.7	18.3	18.1
Ultimate Elongation (%)					
	324	406	379	394	362
Shore A Hardness-10 sec.					
	72	73	74	73	74
100% Modulus (MPa)					
	10.3	8.6	8.8	8.0	9.0
Extractability (Percent Weight Loss)					
Hexane	25.5	21.2	22.7	21.9	21.7
Soapy Water	10.2	8.6	9.6	9.2	8.7
Volatility (Percent Weight Loss)					
Fusion Process Volatility					
	1.4	2.3	2.2	3.0	2.5
Oven/Activated Carbon -90°C-24 hr					
	10.1	10.9	11.2	11.6	12.4
Heat Stability @ 10 min. (ΔE)					
	7.5	7.5	7.1	9.0	8.9
Gloss					
	89	92	91	82	78

Table 4. Basic PVC/DINP Plastisol Formulation					
Formulation	A	B	C	D	E
PVC (Geon 121A)	100	100	100	100	100
DINP	60	50	50	40	40
2-Ethylhexyl Benzoate		10		20	
2,4,4-Trimethylpentan-1,3- diol diisobutyrate			10		20
ESO	2	2	2	2	2
Ba/Zn Stabilizer	3	3	3	3	3

Table 5. Basic PVC/DINP Plastisol Screen					
Performance Properties					
Formulation from Table 4	A	B	C	D	E
Brookfield Viscosity @ 20rpm. (Pa.s), 1 day post-mixing					
1 Day	3.3	1.7	1.9	1.1	1.4
Viscosity @ 20 sec.⁻¹ (Pa.s)					
Initial	2.5	1.6	1.8	1.2	1.3
1 Day	4.1	2.5	2.6	1.8	2.1
3 Day	4.3	2.8	2.8	1.9	2.5
Viscosity @ 800 sec.⁻¹ (Pa.s)					
Initial	6.0	3.3	3.9	1.8	2.4
1 Day	6.2	3.8	4.1	2.3	2.5
3 Day	6.3	3.8	4.0	2.4	2.5
Gelation Temperature (°C)					
	75	71	74	67	72
Mechanical Properties					
Low Temperature Flexibility					
	-28°C	-30°C	-28°C	-31°C	-29°C
Tensile Strength (MPa)					
	16.6	15.5	16.6	15.5	16.0
Ultimate Elongation (%)					
	408	404	399	389	369
Shore A Hardness-10 sec					
	67	66	68	65	66
100% Modulus (MPa)					
	7.6	6.8	7.4	7.0	7.4
Extractability (Percent Weight Loss)					
Hexane	33.9	28.9	29.2	25.6	25.7
Soapy Water	4.2	5.9	5.9	5.7	7.3
Volatility (Percent Weight Loss)					
Fusion Process Volatility					
	0.7	1.5	1.4	2.2	2.1
Oven/Activated Carbon -90°C-24 hr					
	3.8	6.5	6.5	8.6	9.1
Gloss					
	80	93	91	88	95