Analysis of semi-volatiles in dried paint films

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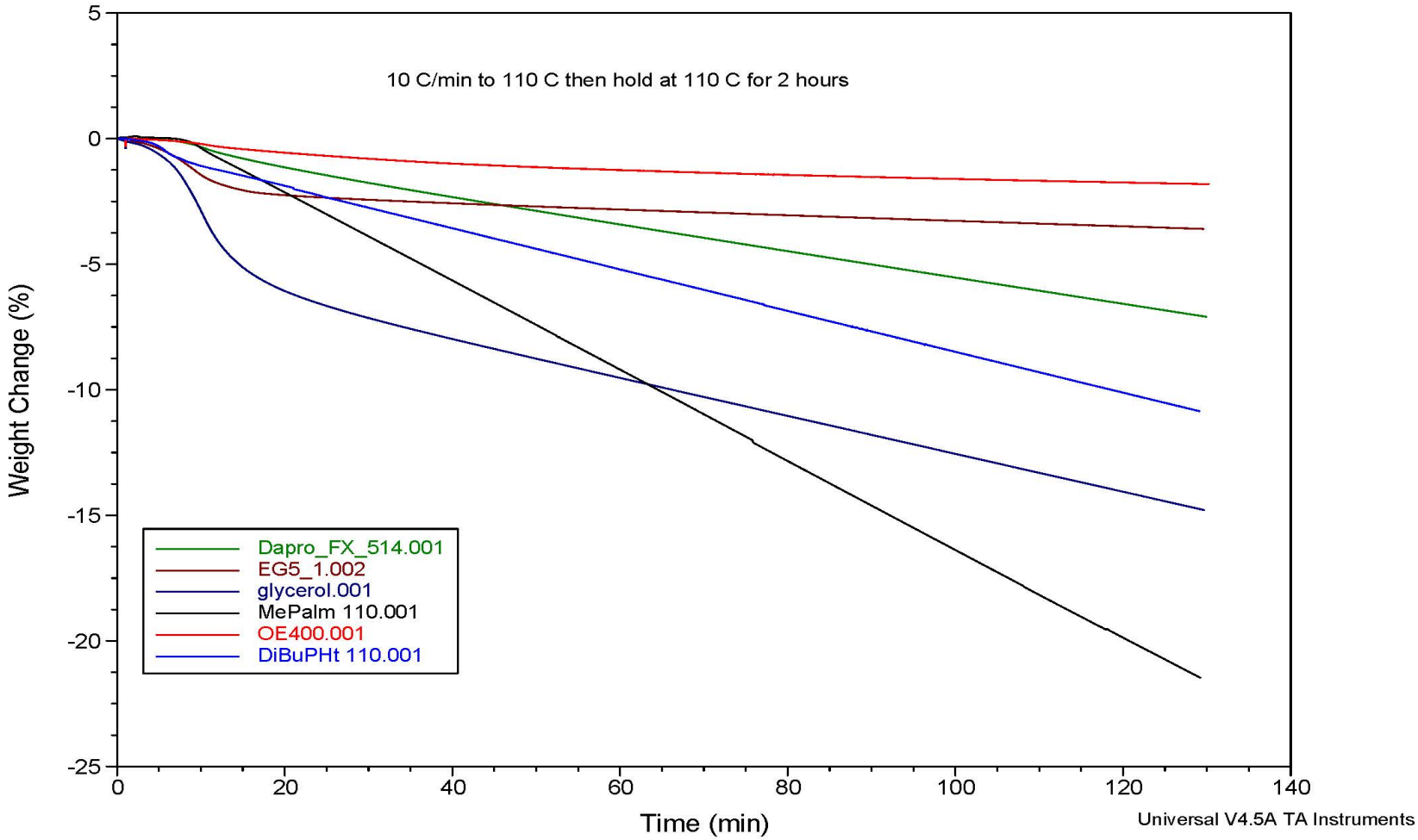
Reasons for study

- Both regulatory agencies and industry desire a method to characterize semi-volatiles
- Study can possibly help classify semi-volatiles based on amounts remaining in films as a function of time or temperature
- ACA has submitted a list of potential semi-volatiles for consideration to SCAQMD

ACA priority semi-volatiles

Vantex-T	Pentaethylene glycol	Poly(neopentyl) glycols
2-ethylhexyl benzoate (Velate 368)	2-amino-1-butanol	Lubrizol GRB3
Polyethylene glycol	2-amino ethanol	Nuosperse AQ100 Nuosperse AQ200 Nuosperse AQ300
Optifilm 400	Soy oil	PEG300 (covered under Polyethylene glycol?)
EPS 9147	HEEU (hydroxyethyl ethylene urea)	Canola oil
Triethylene glycol	2-Hydroxyethyl urea	Tung oil
Tetraethylene glycol	Acrylates	Biocides

TGA Results for Semi-volatiles



Who should develop the method?

- SCAQMD and EPA prefer industry do majority of film extraction method development
- Industry has smaller list of target matrices
- Some companies have suggested “universal” matrices be developed for different classes of coatings
- Preliminary work has been done by some companies, regulatory agencies, and independent laboratories

Summary of proposed method

- A known quantity of the target substance is added to a formulated coating representative of the type of coating for which the substance is designed.
- Solids determinations are done at 110^{o}C for times ranging from 0.5 to 8 hours.
- The films remaining after solids determination are placed in sealed vials and solvent is added to extract any remaining target substance.
- Internal standard is added and the solution is analyzed using ASTM D6886 or AQMD Method 313

Example paint preparation

- A new coalescent to be tested is added at 1% by weight to a near-zero VOC coating known not to contain the new product (the amount added may need to be adjusted)
- The coating sample with the target substance is analyzed using ASTM D6886 or AQMD Method 313
- The amount of the target substance in the coating is verified by comparing to the known formulated value.
- The relative response factor of the target substance should have been determined previously.

Solids samples preparation

- Several samples are prepared according to ASTM Method D2369 for solids determination.
- All samples are placed in an oven at 110°C.
- After 30 minutes, three samples are removed and weighed.
- Three more samples are withdrawn after one hour, two hours and eight hours.
- The fraction solids is determined for each sample.

Analysis of films

- Immediately after the triplicate determination of the solids content of the coating at a particular temperature, the films are removed from the pans and placed in a 40 mL vial and sealed with a septum cap
- A known weight of film is combined with solvent and internal standard in a vial.
- Sample is sonicated and shaken to extract semi-volatiles
- Sample of resulting solution is analyzed by ASTM D6886 or AQMD Method 313 for fraction of each semi-volatile remaining

Sample study

- Commercially available semi-gloss and flat architectural coatings (white) listed as “zero VOC” were purchased
- Paints were analyzed using ASTM D6886 to determine VOC content and identity of any VOCs present
- Based on analysis, three initial semi-volatiles were chosen to add to the paints: Texanol®(TX), Velate 368® (VE368) and dibutyl phthalate (diBuPh)
- DiBuPh (BP 340 C) has volatility similar to methyl palmitate (BP 335 C); TGA shows diBuPh slightly less volatile than MePalm
- Triethanol amine (TEA), 2-amino-2-ethyl-1,3-propanediol (AEPD), tetraethylene glycol (EG4) and pentaethylene glycol (EG5) also studied in semi-gloss paint

Preparation of spiked paints

- 650 grams paint were weighed into 1 pint paint can
- Approximately 1% TX, 0.5 % Ve368 and 0.5% DiBuPh were added to the paint
- The paint and additives were dispersed for 30 minutes using a high-speed paint disperser and the can was sealed
- Before use the paints were shaken for 6 minutes on a shaker
- Paints were analyzed using ASTM D6886

Preparation of paint films

- Preliminary studies showed little useful information obtained from study of film heated for longer than two hours at 110^{o}C
- Samples were prepared using Method D2369 for solids analysis
  - 0.5-1.0 gram of paint added to weighed aluminum pan
  - 3 mL water added and mixture dispersed using paper clip
  - Also tried without water and obtained same results
- Samples heated for 0.5, 1.0 and 2.0 hours then reweighed
- Solids fraction at each time determined

Preparation of film samples

- After cooling, films were removed from pans by peeling or scraping taking care to remove as much film as possible but no aluminum
- Each film after removal was transferred to a tared vial. Film samples typically weighed 0.3-0.5 g.
- Solvent (either acetone or acetone/methanol mixture) containing 1.5 mg EGDE internal standard was added
- Samples were capped and sonicated for 30 minutes then shaken for one hour on vortex mixer.

GC analysis of films

- Samples of film extract solution were analyzed using ASTM D6886. New DB5 column installed and response factors for analytes were determined just prior to measurement.
- Analysis was performed in triplicate and average fraction of each analyte in the solid film sample was determined.
- Fraction in solid film sample multiplied by fraction solids in paint (determined at same heating time) to determine fraction of original analyte in paint remaining in the film.
- Divide fraction remaining in film by fraction in paint to obtain fraction of initial semi-volatile remaining.

Initial results for two spiked commercial paints

Flat Interior Latex Paint			
	fraction initial analyte remaining		
time/hr	TX	VE368	diBuPh
0.5	0.118	0.276	0.962
1.0	0.034	0.084	0.514
2.0	0.005	0.007	0.216

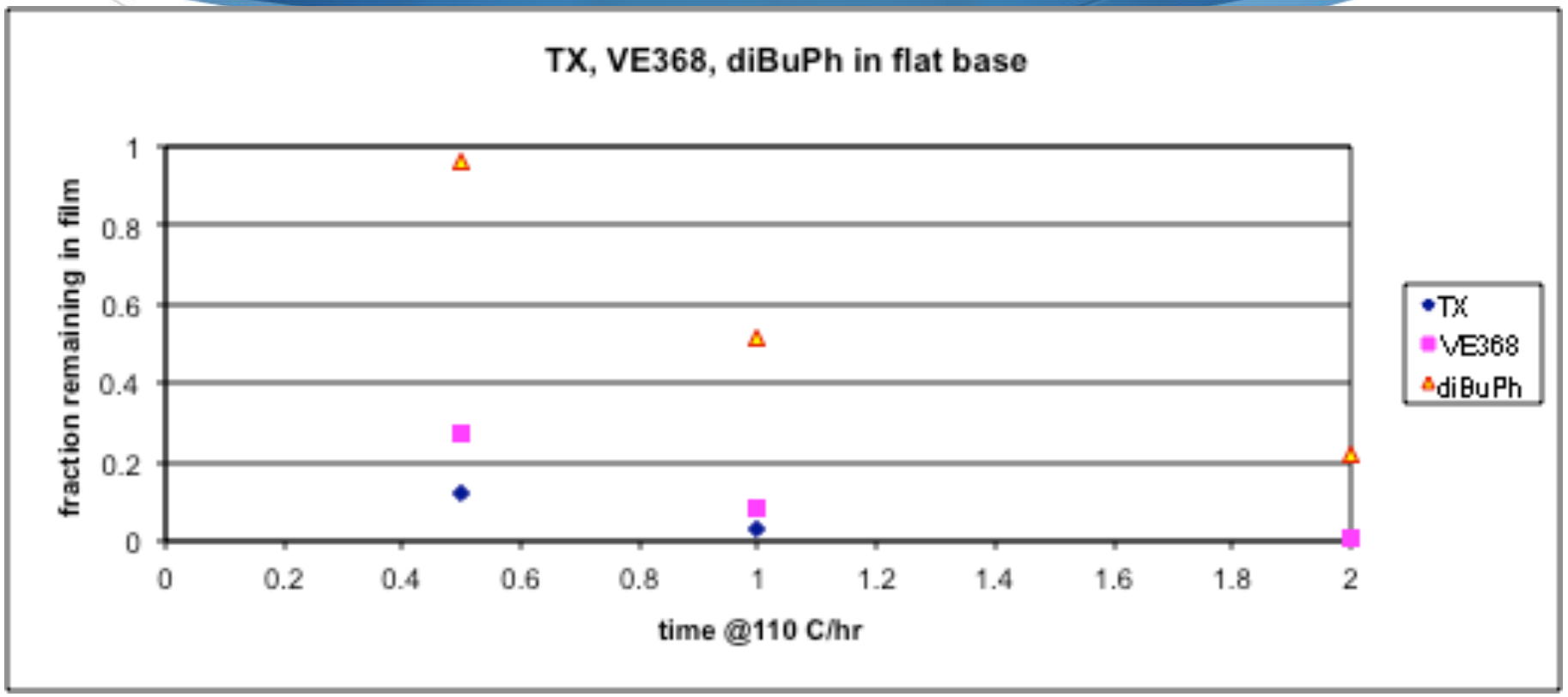
Semi-gloss Interior Latex Paint			
	fraction initial analyte remaining		
time/hr	TX	VE368	diBuPh
0.5	0.302	0.491	0.978
1.0	0.262	0.359	0.842
2.0	0.029	0.036	0.372

Results for amines and polyethylene glycols

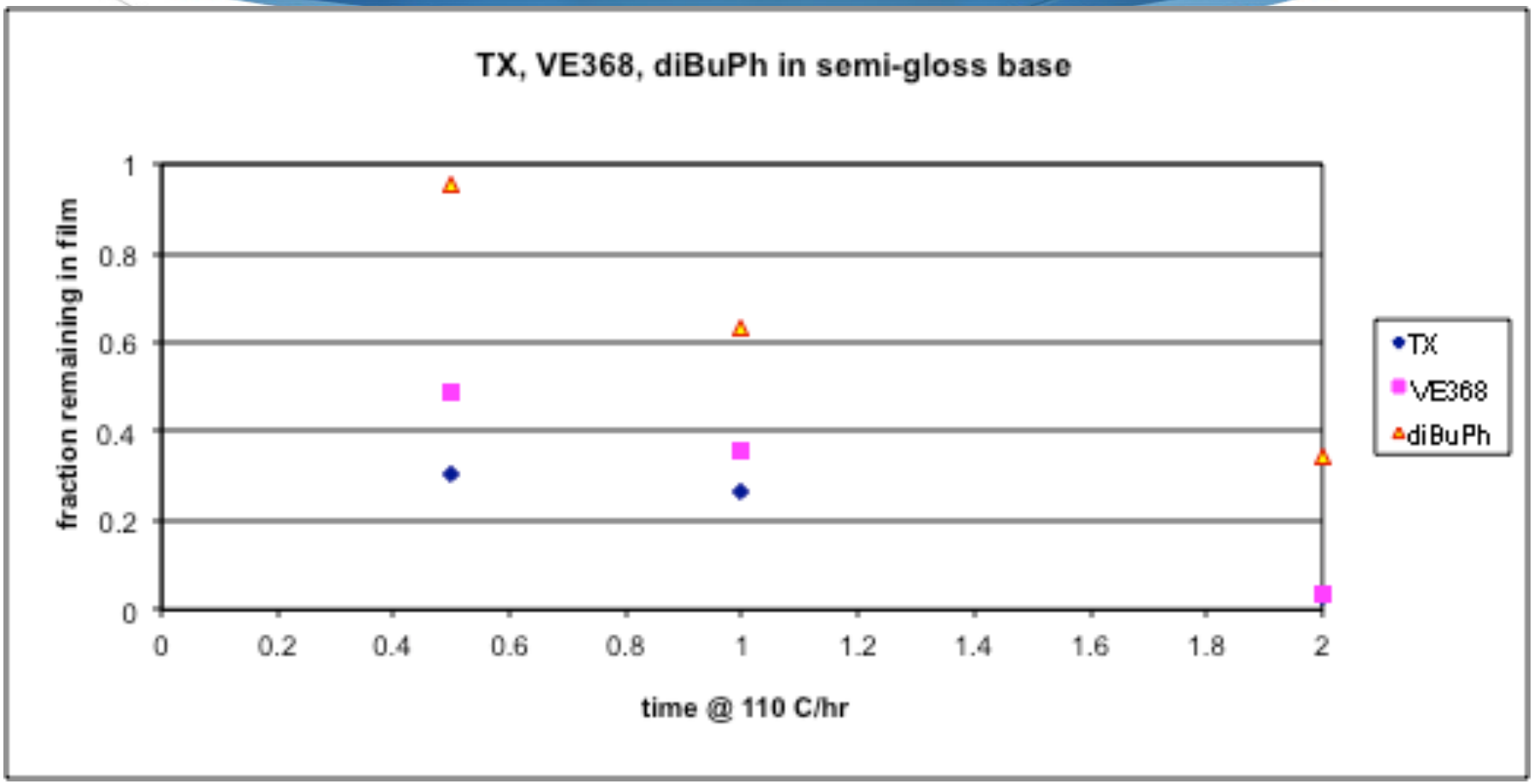
Semi-gloss Interior latex Paint			
	fraction initial analyte remaining		
time/hr	TEA	EG4	DBP
0.5	0.519	0.653	0.893
1.0	0.262	0.195	0.548
2.0	0.015	0.005	0.127

Semi-gloss Interior latex Paint			
	fraction initial analyte remaining		
time/hr	AEPD	EG5	DBP
0.5	0.376	0.920	0.999
1.0	0.153	0.491	0.504
2.0	0.098	0.338	0.320

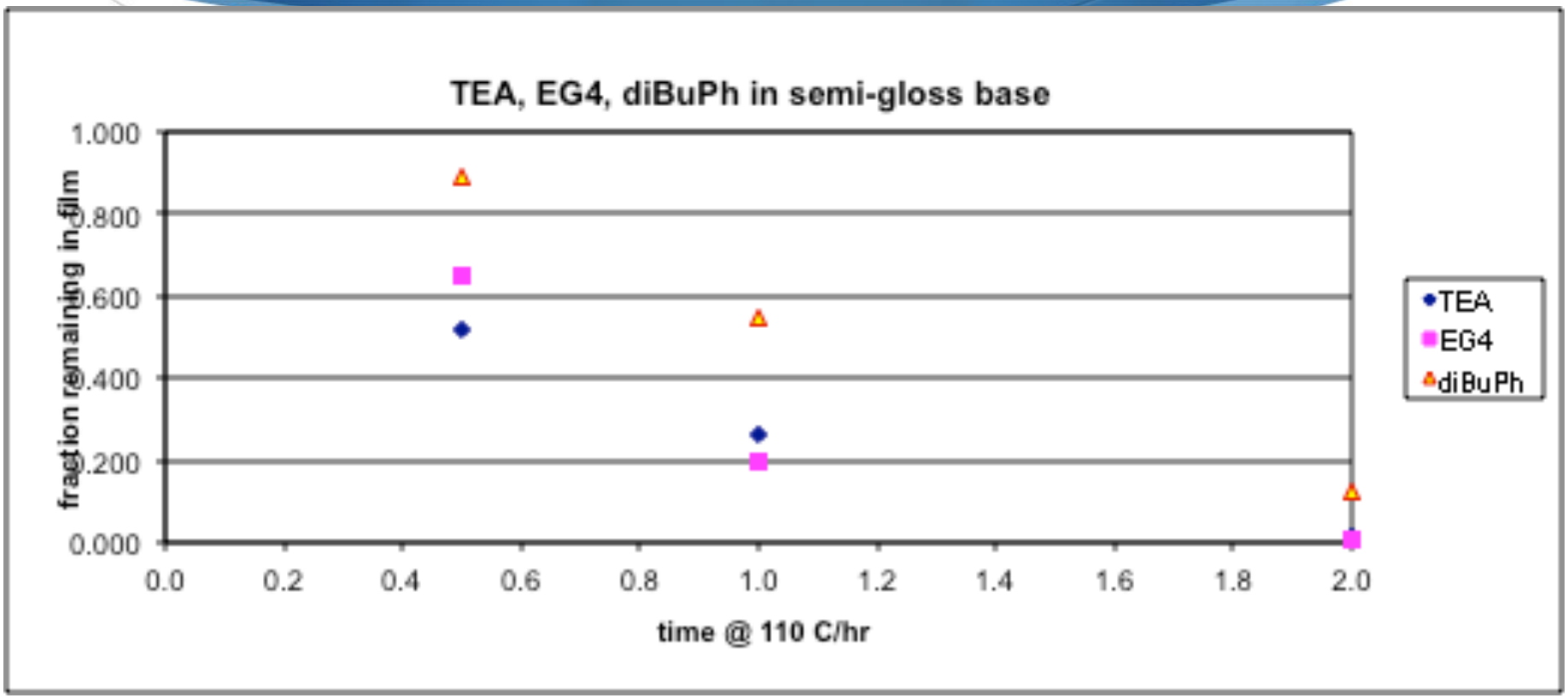
Results for flat latex paint films TX, VE368



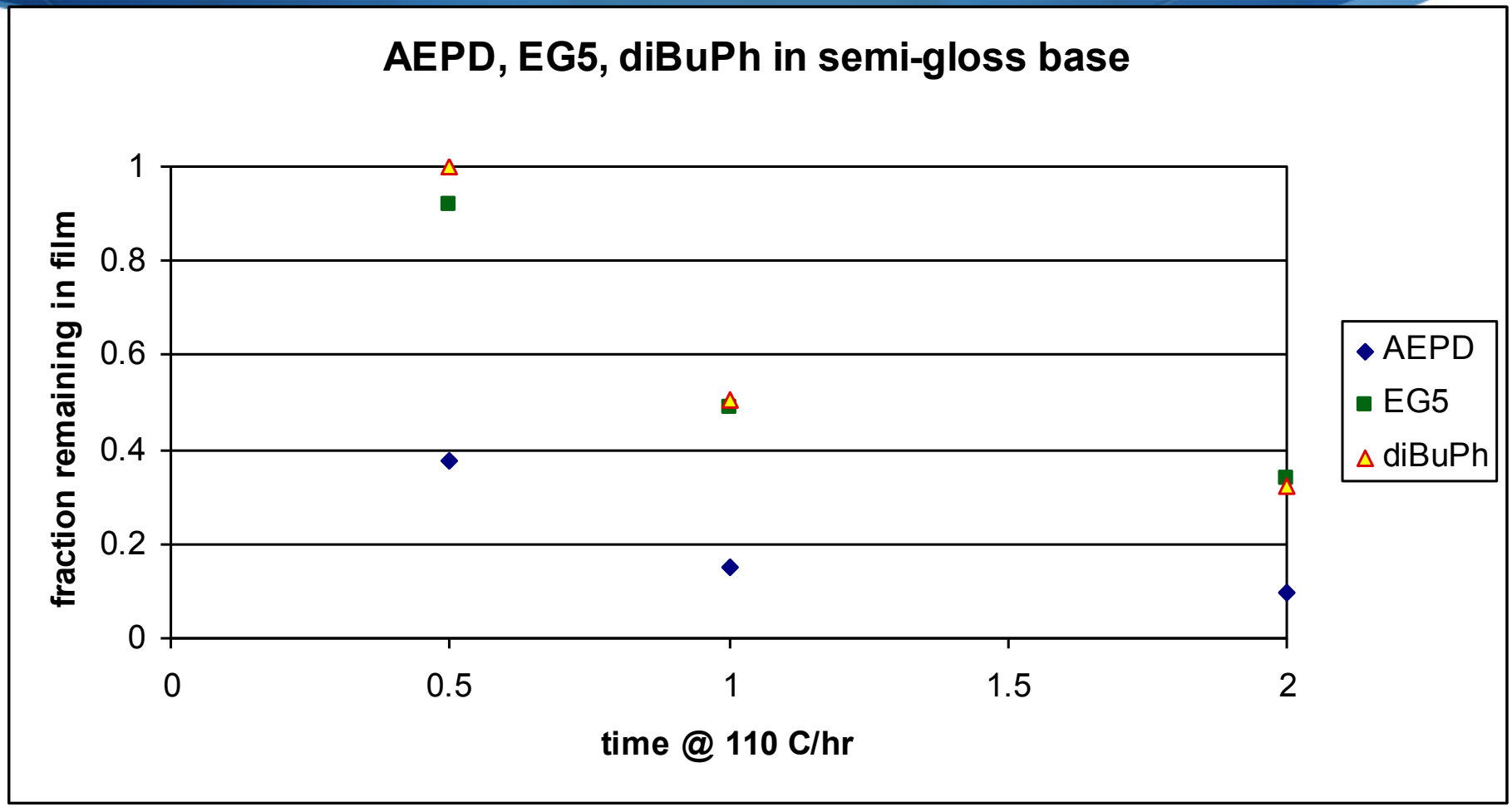
Results for semi-gloss latex films TX, VE368



Results for TEA, EG4



Results for AEPD, EG5



Comments on results

- Decrease in fraction of all semi-volatiles in films with increased heating time
- Larger fractions remained in semi-gloss films than in flat films
- Results are consistent from both types of paint films
- Both qualitative and quantitative statements of relative volatility of these materials in these films can be made
- Pentaethylene glycol shown to have same volatility behavior in film as dibutyl phthalate (classified as non-VOC by method 313).

Future Work

- Similar studies need to be done on other target semi-volatiles
- Need to determine a criterion for judging a material to be non-volatile (or partially volatile?)
- May need to look at other temperatures/times or extracting solvents
- Need industry and regulatory agencies to give their input