Lubricating Rigid PVC Pipe Formulations
Current Issues and Options

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2012 Uni-Bell Meeting

Typical Rigid PVC Formulation

PVC Resin

Tin Stabilizer

Lubricants

Calcium Carbonate

Pigments

Rigid PVC Lubricants

- Paraffin waxes have been used for more than 40 years to lubricate rigid PVC.

- Large volume PVC applications using paraffin waxes as the primary lubricant include:

  - Pipe
  - Vinyl Siding
  - Vinyl Windows
  - PVC Fencing
  - PVC Boards

Typical Lubricant System

- Paraffinic Hydrocarbon Wax
  - Refined from crude or synthetic based on ethylene or methane
  - Typical $C_{32}H_{66}$
- Calcium Stearate
  - Calcium salt of acid from natural fats and oils
  - $Ca(C_{18}H_{35}O_2)_2$
- Oxidized PE Wax
  - Ethylene based
  - $C_{100+}H_{200+}O_?$

Early R&D Work

- A range of Fully Refined Paraffin Waxes were evaluated in the 1960's in the search for an effective, low cost, rigid PVC lubricant system.

- The first wax approved was Aristowax 165, a high melting point, straight cut, fully refined, intermediate wax.

Refining Paraffin Waxes – 1970

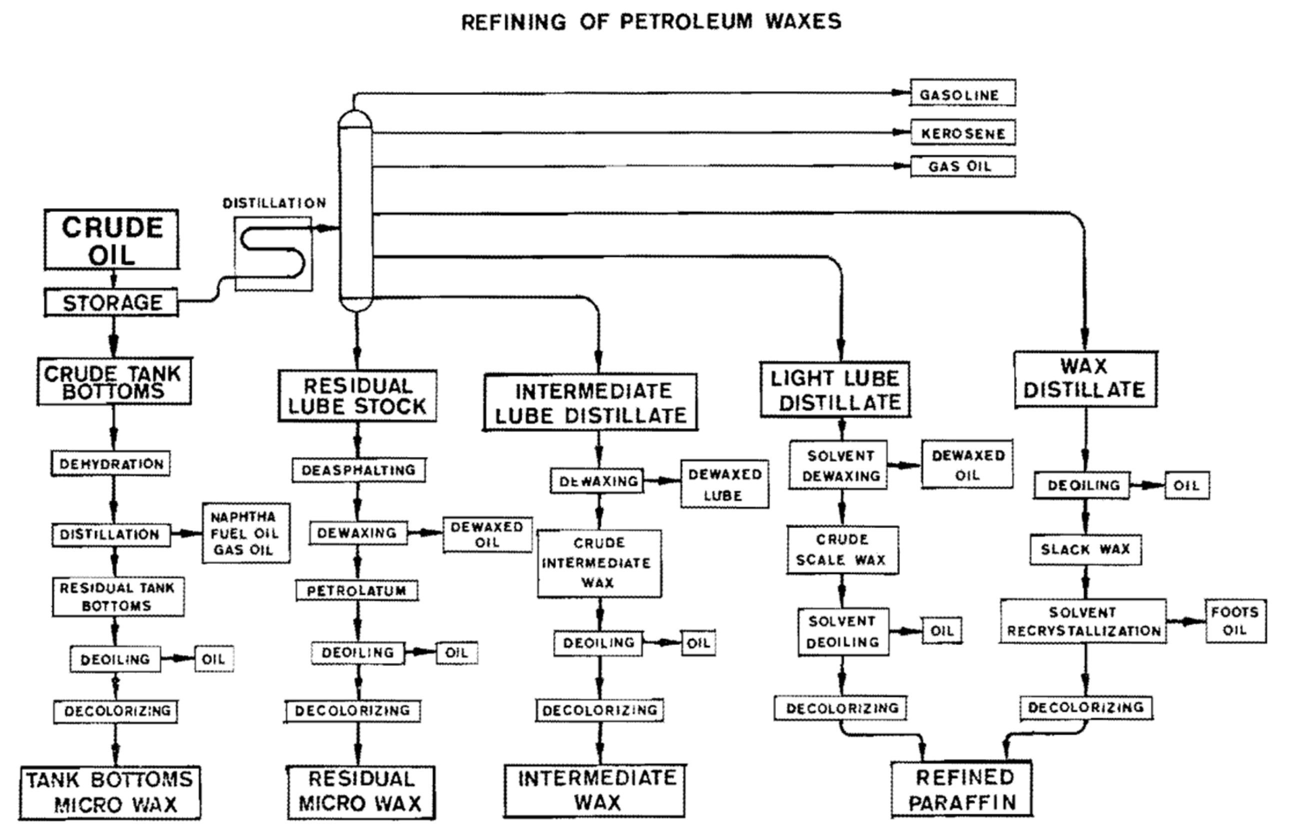

FIGURE 1

[10]

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Reference: Wax Technology, CSMA, 1975

165 Waxes

- 165 waxes are mixtures of branched and straight chain paraffin molecules:
  - Normal Straight Chain Content
    - $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
  - Branched or "Non-normal" Content
    - CH_3 (branch)
    - $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_1CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_1CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
    - CH_2
    - CH_2
    - CH_3
  - Over 1,000,000 different C_{32+} H_{66+} molecular structures are possible.

Effect of Wax Molecule Size on Rheology

Carbon Number	Fusion Time	Fusion Torque	Equil. Temp
26	166 sec	21.3 Nm	>195°C.
32	352 sec	15.2 Nm	188°C.
40	2,120 sec	10.1 Nm	188°C.
100+ (PE Wax)	182 sec	18.9 Nm	>195°C.

C_{26} more soluble in rigid PVC. C_{100+} insoluble in rigid PVC.

Early Paraffin Waxes – Late 60s

- Aristowax 165 was identified by B. F. Goodrich as the early paraffin wax lubricant standard. Aristowax 165 was refined by Union Oil Company of California.
- Sunolite 160 soon followed as a second source. Sunolite 160 was refined by Sun Oil Company in Oklahoma.
- Other sources: Rosswax 165, Advawax 165

1970s

- The PVC industry quickly outgrew the supply of fully refined 165 paraffin waxes.
- Hoechst offered XL-165, a blend of paraffin waxes and microwaxes.
- Olefin waxes very similar to 165 paraffin became available.
- Hoechst offered XL-165 SB, a blend of paraffin and olefin waxes.
- Hoechst became the predominate North America supplier of paraffin waxes used in rigid PVC.

Refining Paraffin Waxes – 1970

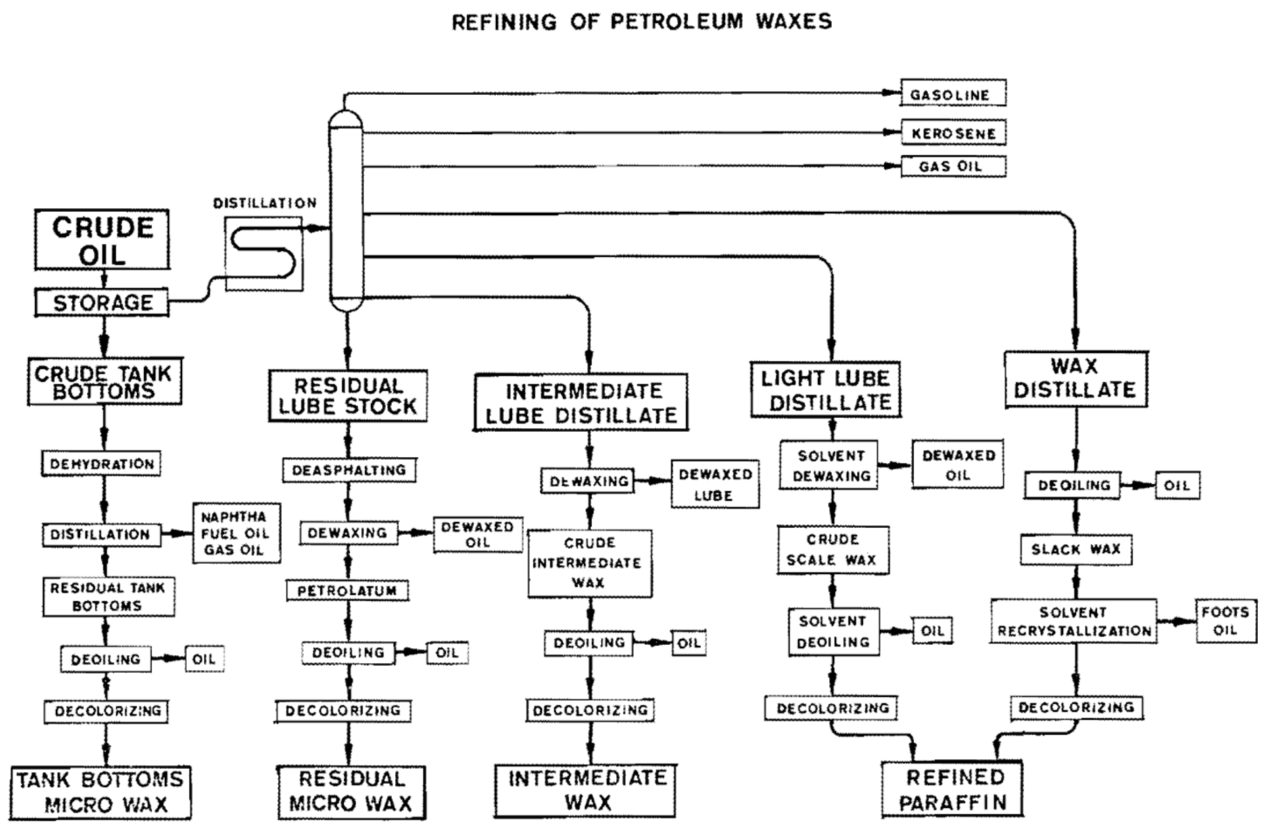

FIGURE 1

[10]

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Reference: Wax Technology, CSMA, 1975

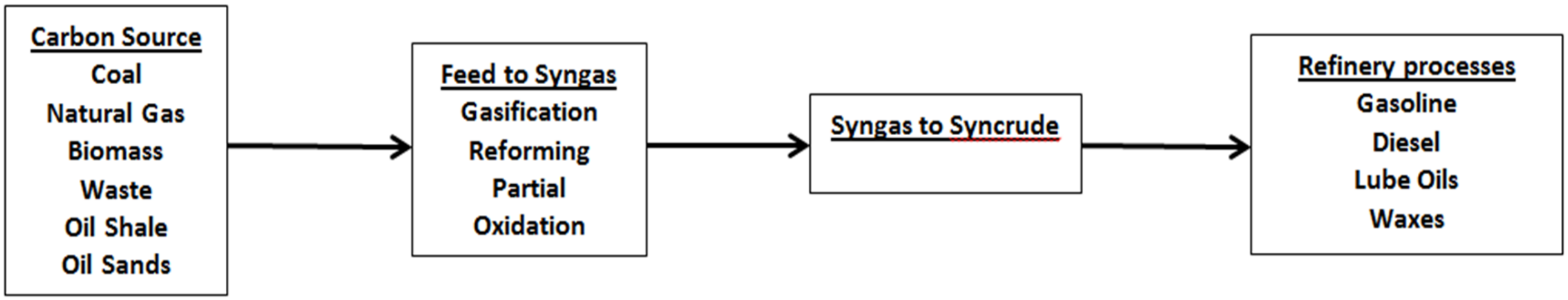
1980s

- New source of fully refined high melting paraffin waxes became available in Louisiana.
- China began exporting large quantities of paraffin waxes.
- New catalytic dewaxing technology allowed refineries to opt out of wax production. Some refineries stop making wax.

1990s

- Chinese wax exports expand.
- More North American refineries opt out of wax.
- Production starts of Fischer-Tropsch waxes in Malaysia.
- Olefin wax production expands.
- Explosion shuts down Fischer-Tropsch wax plant in Malaysia.

Fischer-Tropsch Process Overview



Key Reaction

$$(2n+1)\ H_2 + n\ CO \rightarrow C_nH_{(2n+2)} + n\ H_2O$$

Reference: Fischer-Tropsch Refining, de Klerk, Wiley-VCH, 2011

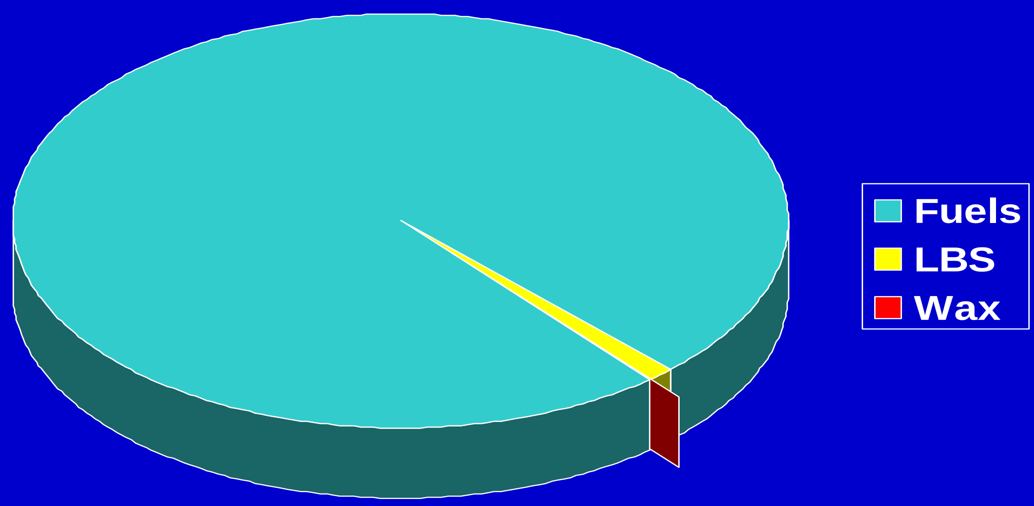
2000s

- New olefin wax production in Quatar.
- North American refineries continue to opt out of wax.
- Malaysian Fischer-Tropsch production resumes.
- Chinese imports continue to grow.
- Hurricanes Katrina and Rita impact our industry.
- Imported waxes become price leaders.

PUTTING WAX IN PERSPECTIVE

SOURCES: OIL & GAS JOURNAL, LUBES 'N GREASES, IEA, MY ENERGY DATABASE

2006 GLOBAL REFINING CAPACITY – 99% FUELS



LUBE BASESTOCKS ARE ONLY 1% OF GLOBAL REFINING CAPACITY

WAXES ARE 0.1% OF GLOBAL REFINING CAPACITY

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Slide courtesy of Amy Claxton of My Energy

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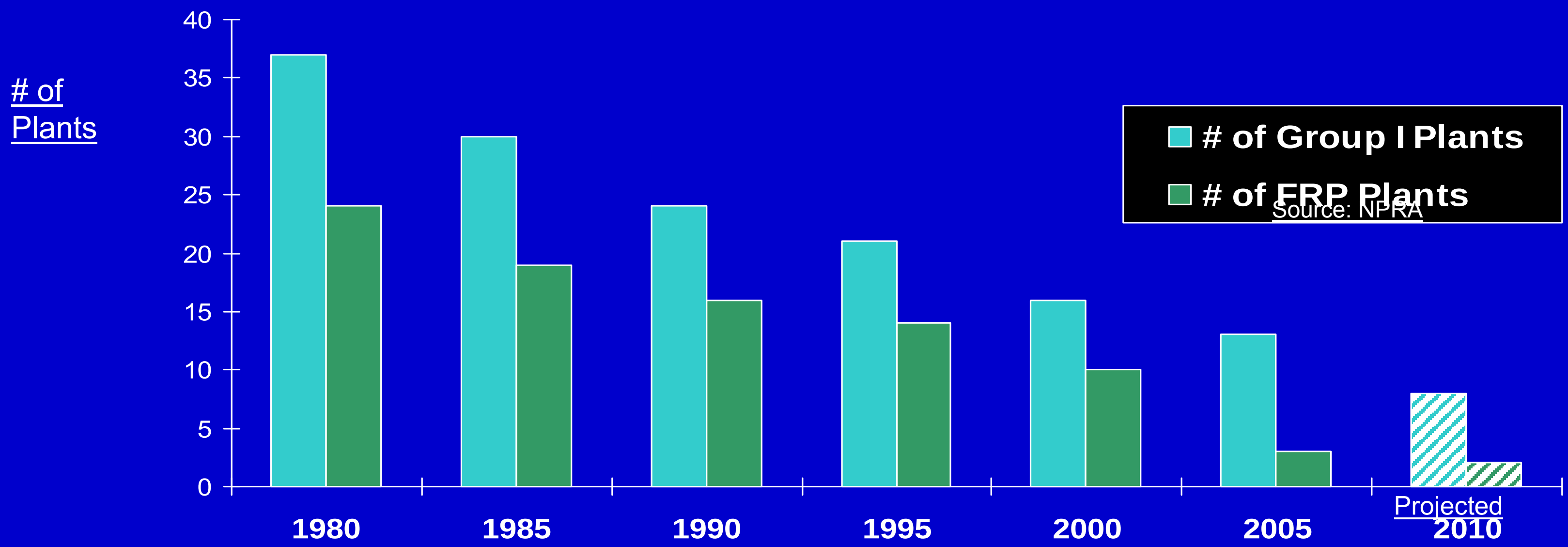
Slide Courtesy of Amy Claxton, My Energy

REFINING TREND #2:

WHY IT MATTERS: GROUP I LUBE PLANT QUALITIES ARE DEFENSIVE

EXAMPLE: NORTH AMERICAN GROUP I LUBE PLANTS



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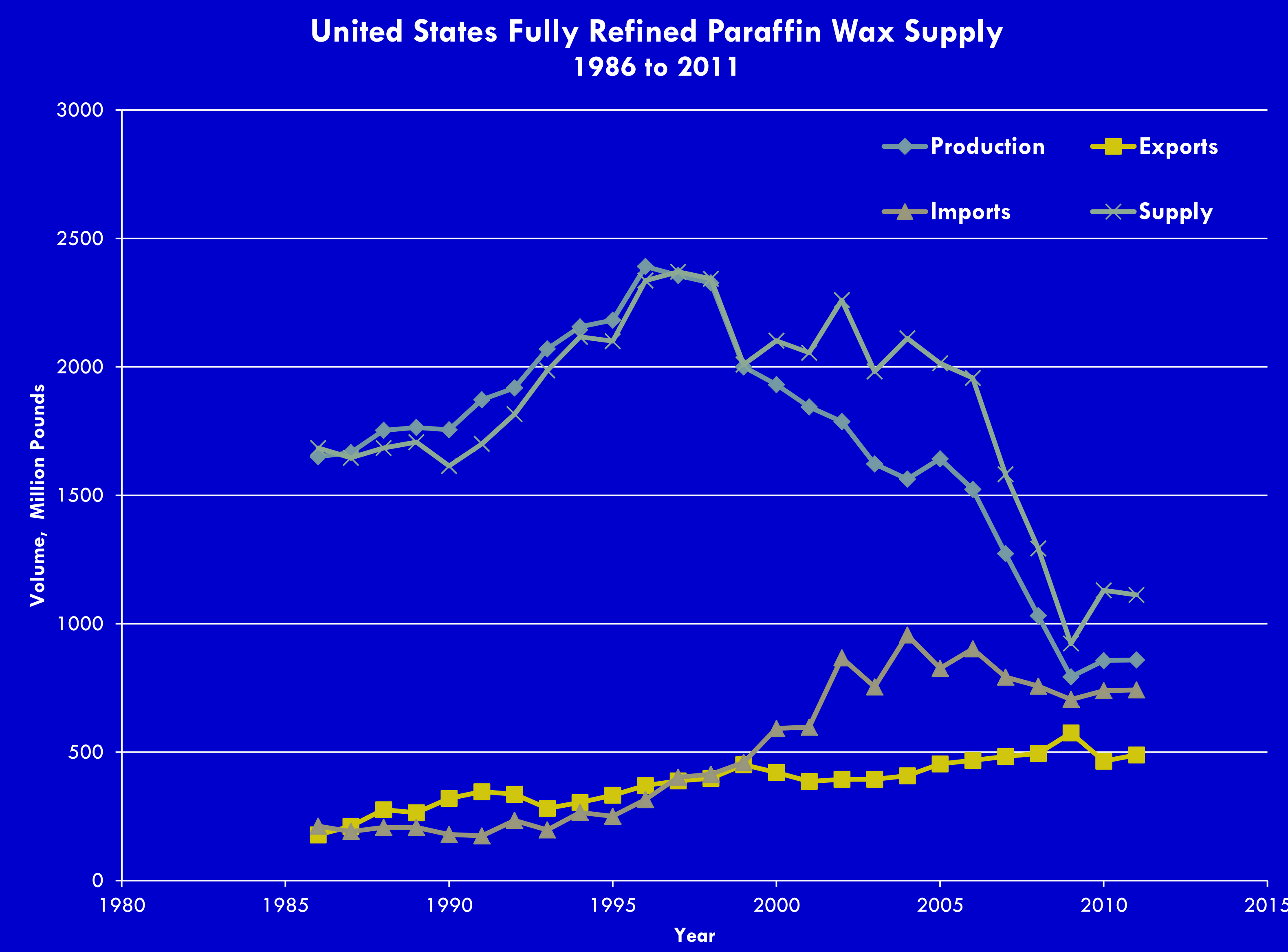

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Graph based on data from Wax Data

Where are we today?

- Paraffinic hydrocarbon wax supplies have been sufficient to meet the needs of the rigid PVC Industry.
  - Refined wax capacity in USA has stabilized
  - Synthetic olefin wax supply is large and stable
  - Imports have grown

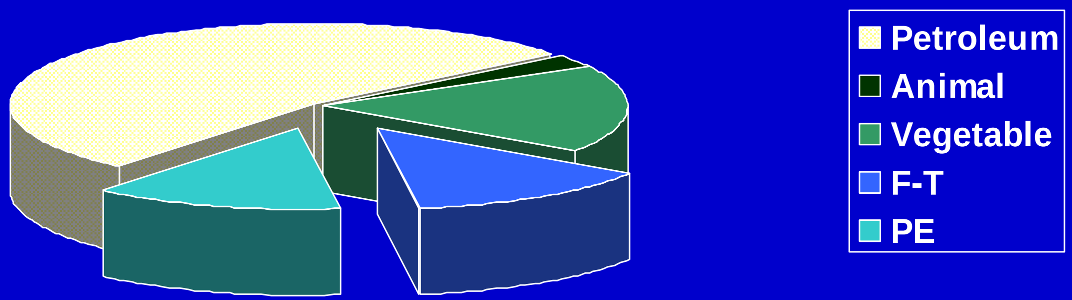
  - Supply and demand are reasonably balanced. However:

Where are we today?

However…….

- The amount of rigid PVC processed in North America has tumbled since 2008 and remains at historically low levels.
- If the rigid PVC industry expands rapidly, current wax supplies may become tight or escalate in price.

DECLINES IN CONVENTIONAL PETROLEUM WAX SUPPLIES . . .



BRING ADDITIONAL OPPORTUNITIES FOR NATURAL AND SYNTHETIC WAXES

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Slide courtesy of Amy Claxton of My Energy

The Outlook

- Currently there are adequate supplies of paraffin wax.
- If current rigid PVC volumes double or triple, new lubricant technology will help insure adequate supplies.
- Solutions
  - The use of hydrocarbon waxes outside the current limits of the PPI Specification for paraffinic hydrocarbon waxes.
  - The use of bio-based synthetic waxes.

The Challenge

- 165 waxes are hard to replace part for part.
  - PPI Range Composition usage range limits are 0.80 to 1.50 phr.
- Higher usage levels of suitable molecules may be necessary to optimize their performance and economics.
- Approval of higher usage levels of suitable molecules in the PPI PVC Pipe Range Composition.
- Delivering products in an easy to handle form.
- Maintaining equal or better economics.

Synertive® RX-2975

- A lubricant system containing a refined domestic paraffin wax together with calcium stearate and oxidized polyethylene wax.
  - Abundant paraffin wax source.
  - Better economics.
  - Can be handled using the same equipment.
  - Very similar processing characteristics.
  - Already NSF and PPI approved in PPI PVC Pipe Range Composition.

PPI PVC Range Composition

NSF Version 24.0

Issued February 2011

Supplement To Table 10B-Functionally Equivalent Ingredient Package

Source or Vendor	Ingredient Trade Designation	Use Level (phr)	Limitations
Rheogistics LLC	Synertive® RX-2975	1.50 – 2.24 phr	see note below

Note: Synertive® RX-2975 contributes the following at 2.24phr: 40.67% Calcium Stearate, 100% Paraffin Wax and 45.37% Polyethylene Wax

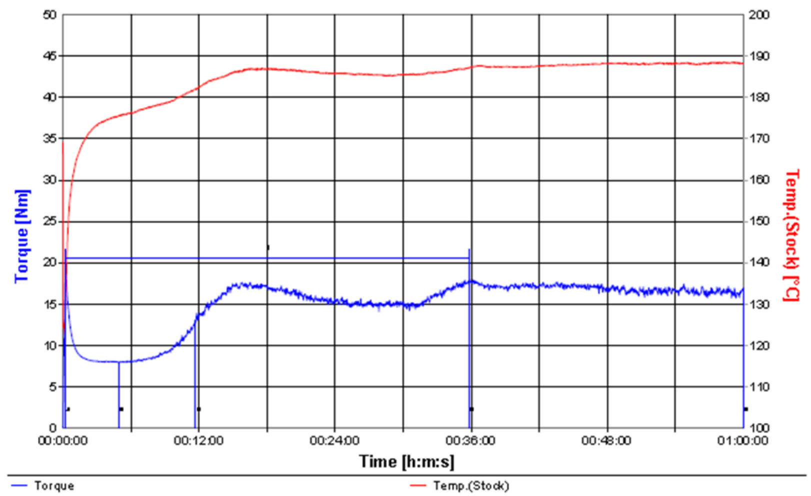
*This Report is not a complete formulation. This report supplements NSF Version 24.0 issued February 2011

------------------------------ (Program Office Authorization) Date: -----/-----/-----

BRABENDER® Plastogram
PLASTI-CORDER and Mixer Measuring Head
Fusion Behaviour / Version 3.1.6

Test Conditions

Order	: BRABENDER	Speed :	60 1/min
Operator	: TCN	Mixer Temp. :	175 °C
Date	: 3/23/2012 10:47	Start Temp. :	169 °C
Drive Unit	: Intelli Torque 7150	Meas. Range :	50 Nm
Mixer	: Roller Type 6 Elect	Damping :	3
Loading Chute	: Manual +5 kg	Test Time :	60 min
Sample	: RX-2975	Sample Mass :	65.0 g
Additive	: STANDARD	Code Number :	



Name		Time [h:m:s]	Torque [Nm]	Stock Temp. [°C]
Loading Peak	A	00:00:16	19.6	131
Minimum	B	00:04:56	7.9	176
Inflection Point	G	00:11:42	12.6	182
Maximum	X	00:35:50	17.6	187
End	E	01:00:00	16.9	188

Integration / Energy

Loading Peak	to Minimum	A - B	15.8	[kNm]
Minimum	to Maximum	B - X	167.5	[kNm]
Maximum	to End	X - E	153.6	[kNm]
Loading Peak	to Maximum	A - X	183.2	[kNm]
Loading Peak	to End (W)	A - E	336.8	[kNm]
Specific Energy(W/Sample Mass)			5.2	[kNm/g]
Gelation Area above B		B - X	75.5	[kNm]

Results

Fusion Time t	A - X	00:35:34	[h:m:s]
Gelation Speed v		4.0	[Nm/min]

Page : 1 File : RX-2975 STND

C-900 Mid-wall after Methylene Chloride Exposure

C-900/905 PVC Pipe

- Complex Process Induced Morphology
  - Inner skin of well fused material
  - Outer skin of well fused material
  - Middle wall retains particle structure of PVC resin
    - Middle wall impacted by rheological behavior

Shift in Synertive® RX-2975 rheology may benefit middle wall

Longstanding Alternate Lubricant Systems for Rigid PVC

- Montan Waxes – the earliest standard
  - Hoechst Wax E & OP
  - Esters of Montanic acid
  - Derived from coal
- Fatty acid esters pioneered by Henkel
  - Derived from natural oils and fats
- Amide waxes
  - Ethylene bisstearamide wax
  - Majority of product derived from natural oils and fats

Sources of Esters

Biodiesel sources include soybean oil, tallow (rendered mutton or beef fat), palm oil and used cooking oil.

Problem: Competing with subsidized bio-diesel for raw materials.

Reference: Lubes'n'Greases, November/December 2009

Dr. Diesel & Us

Rudolph Diesel Preferred Our Fuel

The history of the diesel engine begins in Germany with the invention of the engine by Rudolph Diesel. Rudolph Diesel ran his engine at the 1900 World's Fair on pure peanut oil.

His intention in his engine design was to make an engine that could be run cheaper by using vegetable oil instead of the new petroleum oil being used for cars. It would also enable farmers to produce their own "fuel" from their crops for their machinery. However, the rapidly growing petroleum industry quickly made their version which was cheaper and would remain so for decades. Today however, fuel costs are obviously much higher and thus Mr. Diesel's original intent for his engine design can finally be realized by the masses.

Synertive® RX-100 and RX-300 Versatile Chemistry

- Hybrid ester based lubricants, free of fully refined paraffin wax.
- Abundant supplies of raw materials.
- Competitive or better economics.
- Very similar handling and processing characteristics.

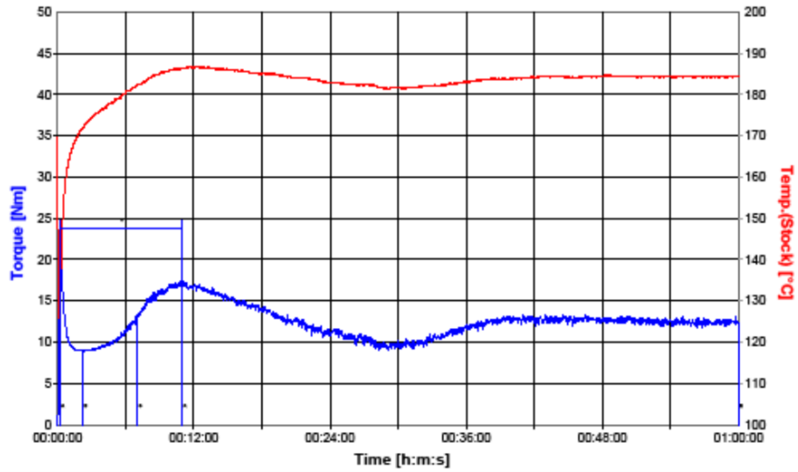
BRABENDER® Plastogram

PLASTI-CORDER and Mixer Measuring Head

Fusion Behaviour / Version 3.1.6

Test Conditions

Order	: BRABENDER	Speed	:	60 1/min
Operator	: TCP	Mixer Temp.	:	175 °C
Date	: 1/20/2012 09:56	Start Temp.	:	170 °C
Drive Unit	: Intelli Torque 7150	Meas. Range	:	50 Nm
Mixer	: Roller Type 6 Elect	Damping	:	3
Loading Chute	: Manual + 5 kg	Test Time	:	60 min
Sample	: RX-100 Product Development	Sample Mass	:	65.0 g
Additive	: Rx-165 at 1.50 phr	Code Number	:	0.75 phr Calcium Stearate



Name		Time [h:m:s]	Torque [Nm]	Stock Temp. [°C]
Loading Peak	A	00:00:14	22.7	131
Minimum	B	00:02:14	9.0	172
Inflection Point	G	00:07:02	13.1	182
Maximum	X	00:10:58	17.2	187
End	E	01:00:00	12.4	184

Integration / Energy

Loading Peak	to Minimum	A - B	8.2	[kNm]
Minimum	to Maximum	B - X	41.9	[kNm]
Maximum	to End	X - E	230.0	[kNm]
Loading Peak	to Maximum	A - X	50.1	[kNm]
Loading Peak	to End (W)	A - E	280.0	[kNm]
Specific Energy(W/Sample Mass)			4.3	[kNm/g]
Gelation Area above B		B - X	12.4	[kNm]

Results

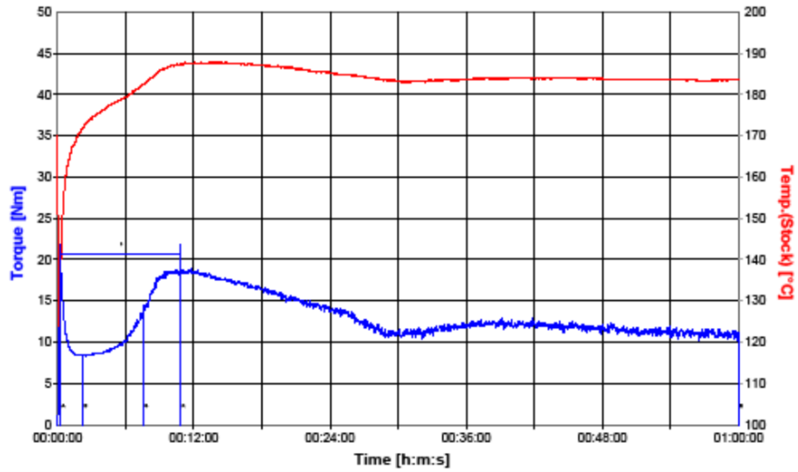
Fusion Time t	A - X	00:10:44	[h:m:s]
Gelation Speed v		2.9	[Nm/min]

BRABENDER® Plastogram

PLASTI-CORDER and Mixer Measuring Head
Fusion Behaviour / Version 3.1.6

Test Conditions

Order	: BRABENDER	Speed :	60 1/min
Operator	: TCP	Mixer Temp. :	175 °C
Date	: 1/20/2012 12:41	Start Temp. :	170 °C
Drive Unit	: Intelli Torque 7150	Meas. Range :	50 Nm
Mixer	: Roller Type 6 Elect	Damping :	3
Loading Chute	: Manual + 5 kg	Test Time :	60 min
Sample	: RX-100 Product Development	Sample Mass :	65.0 g
Additive	: Rx-100 at 1.80 phr	Code Number :	0.75 phr Calcium Stearate



Name		Time [h:m:s]	Torque [Nm]	Stock Temp. [°C]
Loading Peak	A	00:00:16	19.8	136
Minimum	B	00:02:14	8.4	172
Inflection Point	G	00:07:34	13.6	183
Maximum	X	00:10:50	18.8	188
End	E	01:00:00	11.1	184

Integration / Energy

Loading Peak to Minimum	A - B	7.5	[kNm]
Minimum to Maximum	B - X	41.0	[kNm]
Maximum to End	X - E	241.1	[kNm]
Loading Peak to Maximum	A - X	48.5	[kNm]
Loading Peak to End (W)	A - E	289.5	[kNm]
Specific Energy(W/Sample Mass)		4.5	[kNm/g]
Gelation Area above B	B - X	13.9	[kNm]

Results

Fusion Time t	A - X	00:10:34	[h:m:s]
Gelation Speed v		3.2	[Nm/min]

Rheogistics®

2012 Bulk Storage Expansions

2012 Uni-Bell Meeting

Rheogistics®

Picayune, Mississippi USA Plant

Started operating in June 2003

Conclusions

- The lubrication requirements of the rigid PVC industry have been met seamlessly despite major changes in the wax industry.
- New products like Synertive® RX-2975 and RX-100 will help to insure long term requirements are satisfied as economically as possible.
- Rheogistics is investing today in both current and new products to meet the long term needs of the rigid PVC pipe industry.

Thank You!

Rheogistics®

Better Rigid PVC