

THE CHALLENGES OF REPLACING EXISTING COMPOUNDING INGREDIENTS BECAUSE OF LEGISLATION

Warren Febery

Clwyd Compounders Ltd, Unit 1, Gardden Industrial Estate, Ruabon, Wrexham, LL14 6RG, UK

BIOGRAPHICAL NOTE

Warren Febery, BSc Hons Polymer Science and Technology, has 18 years experience as a technologist in the rubber industry. Currently, he is a technologist at Clwyd Compounders, and previously with Bull Rubber.

ABSTRACT

This paper will introduce the challenges faced by Custom Compounders in dealing with replacing raw materials due to either legislation, health and safety or supply changes. This has become more apparent with the forthcoming WEEE and RoSH directives that we must all be aware of. At Clwyd Compounders we aim to be proactive when dealing with these issues, and have learnt from previous experiences the difficulties that can be encountered.

The challenge as a compounder is not just to identify chemically suitable alternatives but to fully assess that they do not compromise the myriad of down stream processes or specifications. In many cases expensive tooling and processes, will already exist, which have been designed around the existing formulations.

The paper will use as examples Clwyds experience of replacing Ethylene Thiourea (ETU) and Di-Octyl Phthallate (DOP), both of these ingredients are known to have associated health risks. These examples will be fully detailed in two case studies giving test data generated in our laboratory, showing the physical properties of the new formulation Vs the existing formulation. Other areas that will be considered are bin stability (shelf life) and down stream processing.

Clwyd Compounders Ltd is a specialist rubber compounder based in the UK, founded in 1979 with the aim of providing a total service to rubber compound users. The company now employs a total of 53 people including 3 fully qualified rubber technologists. The factory houses state of the art compounding facilities, mills, internal mixers and a dedicated clean room for speciality elastomers. There is a fully equipped laboratory for compound development and quality control.

At Clwyd Compounders we offer the full range of compounded elastomers including Natural Rubber at one end of the spectrum and Silicone and Perfluoroelastomers at the other (totalling approximately 1200T/PA).

Our customer base also covers a wide range including the engineer wanting to manufacture rubber parts for there own use, engineering based custom moulders, large users who buy their speciality compounds from Clwyd and large users withdrawing from compounding themselves. We have seen a trend over recent years where companies who once compounded for internal use are restructuring and concentrating on manufacturing the finished product and outsourcing the compound.

Each of our customers (approx. 250) requires a different level of technical support ranging from full compound selection, development and manufacturing advice to those with their own technologists needing infrequent support. What ever the customers own technical abilities we endeavour to keep them up to date with current legislation e.g. WEEE & RoSH, new product e.g. Nano particle FKM developments and material withdrawals e.g. Keltan™ 4802 where appropriate.

The Company's products find their way into a wide variety of end use applications and markets including automotive fuel systems, aerospace seals, North Sea oil and many more. Many of these compounds have been designed and developed by our technologists.

Keltan is a registered trademark of DSM

Formulations developed for specific end uses in partnership with customers are held exclusively for that customer. Also formulations developed by the customer and brought to Clwyd for mixing are held exclusively. We have developed a numbering system at Clwyd to ensure both Clwyd and the customer understands which compounds are exclusive. The remaining (approx.) 75% of formulations are Clwyds own intellectual property that has been developed over the years. Many of them used by multiple customers with various manufacturing methods and a myriad of end products. These compounds are often adjusted to match exact customer needs and specifications, at this stage if appropriate they can be given a unique preparation number. Currently we have 5000 plus active formulations i.e. formulations taken in the last 12mths and up to 12000 archived. To enable Clwyd to offer the range of formulations in the required quantities many of the formulations are based on our own internal master batches, this again means material changes can have unforeseen repercussions as the same raw materials go into so many formulations and end products.

REASONS FOR MATERIAL CHANGES

LEGISLATION

There are two main drivers with regards to legislation at the current time GADSL (Global Automotive Declarable Substance List) and WEEE, RoSH with GADSL being the largest.

GADSL is a substance list put together by representatives from the automotive, automotive parts supplier and chemical / plastics industries who have organised the Global Automotive Stakeholders Group (GASG). The purpose of GASG is to facilitate communications and exchange of information regarding the use of certain substances in automotive products. GADSL replaced ILRS in May 2005 and became the primary reference list of declarable substances to be used in conjunction with IMDS. The GADSL list contains materials under two main categories of P prohibited: A substance designated "P" is either prohibited by regulation for use in certain applications or may not exceed regulated threshold limits, and D declarable: A substance designated "D" must be declared if it exceeds the defined threshold limits. Designation "D" does not necessarily mean that the substance is prohibited from being used in vehicle parts or is to be deselected from use. Some materials can be designated P/D this is dependant on end use. Declaration thresholds are designed by specific application. Reason codes have also been developed and are present next to the material on the list, to explain why a material has been included in the GADSL. The GADSL only covers substances that are expected to be present in a material or part that remains in a vehicle at the point of sale. For the suppliers of compound this has meant there need only be one point of reference for all OEM requirements.

WEEE, RoSH

These two directives should be considered together as it would not be deemed cost effective to recycle and reuse without first removing those materials identified as hazardous from the cycle.

Directive 2002/96/EC on Waste electrical and electronic equipment (WEEE): the purpose of this directive is firstly the prevention of WEEE and secondly to promote the reuse, recycling and other forms of recovery of such waste.

Directive 2002/95/EC on the Restriction of the use of certain hazardous substances in electrical and electronic equipment (RoSH): the purpose of this directive is to standardise the laws of member states on RoSH. The directive bans the placing on the EU market of new electrical and electronic equipment containing more than the agreed levels of lead, cadmium, mercury, hexavalent chromium, polybrominated biphenyl (PBB) and polybrominated diphenyl ether (PBDE) flame retardants. This came in to force in the UK 1 July 2006.

Although at Clwyd we do not supply large quantities in to automotive and electronic applications, we need to be up to date for the users of our compounds who do. We also try to be proactive using these lists for other end use applications. We often take the view that simply being on these lists indicates that in time restrictions will be such as to totally prohibit their use. Also being on GADSL may indicate a supplier withdrawal, if the major sector user is no longer permitted to use the material it may no longer be viable to produce, alternatively there may be a large price increase due to reduced demand.

SUPPLIER CHANGES AND MATERIAL WITHDRAWALS

This contributes to over 50% of the material changes at Clwyd. As relatively small users of most of our compounding ingredients we have little influence over their supply. There has been a trend over recent years within our sector for the suppliers to be less visible, their business being handled through distributors e.g. Omya representing Dupont Elastomers in the UK. When the manufacturers were more proactive in the market place if there was to be a material change or withdrawal there would be plenty of notice and opportunity to forward purchase now with little direct contact this is not always the case, this became most noticeable with the withdrawal of Sevacarb MT™, for such an important ingredient we were given very little notice (approx 1 week) or opportunity to stock pile. If we are notified in good time of material changes or withdrawals we usually purchase enough material to cover our usage for 6mths depending on the material, this enables us to orchestrate a smooth transition from one material to another.

INTERNAL INFLUENCES

As indicated when looking at legislation including GADSL we like to be proactive when dealing with our raw material selection and usage. We encourage best practise within our place of work and our customers. An example of this is one of our most recent proactive material withdrawals, as a company we ceased to use ethylene thiourea (ETU) due to being a potent teratogen albeit in rats (see below). On the whole as we only mould for testing purposes this was done for the consideration of our customers' workforce. We have also reduced the use of lead, not only for automotive and electrical applications but across the whole spectrum of industries and are still investing considerable time and effort in to further reductions. Other reductions and ongoing projects include DOP and lead.

The following information was based on a summary of the toxicity of ETU from the "US Environmental Protection Agency" (EPA) web site

Ethylene thiourea is used in the rubber industry as a curative, particularly in polychloroprene compounds and in the production of some fungicides.

No information is available on the acute (short term) or chronic (long term) effects of ethylene thiourea in humans.

In rodents chronically exposed to ethylene thiourea in their diet, effects on the thyroid have been observed.

Ethylene thiourea has been shown to be a potent teratogen (cause birth defects) in rats orally or dermally exposed.

A study of female workers occupationally exposed to ethylene thiourea did not report an increased incidence of thyroid cancer.

In a study by the National Toxicology Program (NTP), an increased incidence of thyroid tumours in rats and thyroid, liver and pituitary gland tumours in mice exposed to ethylene thiourea were noted.

EPA has classified ethylene thiourea as a group B2, probable human carcinogen.

Generally our customers are happy with our material support although there are a few who would rather carry on with existing formulations ignoring the risks. In these instances we have to try and address the obstacles to change, these may include retesting to specifications, processing problems and bin stability issues.

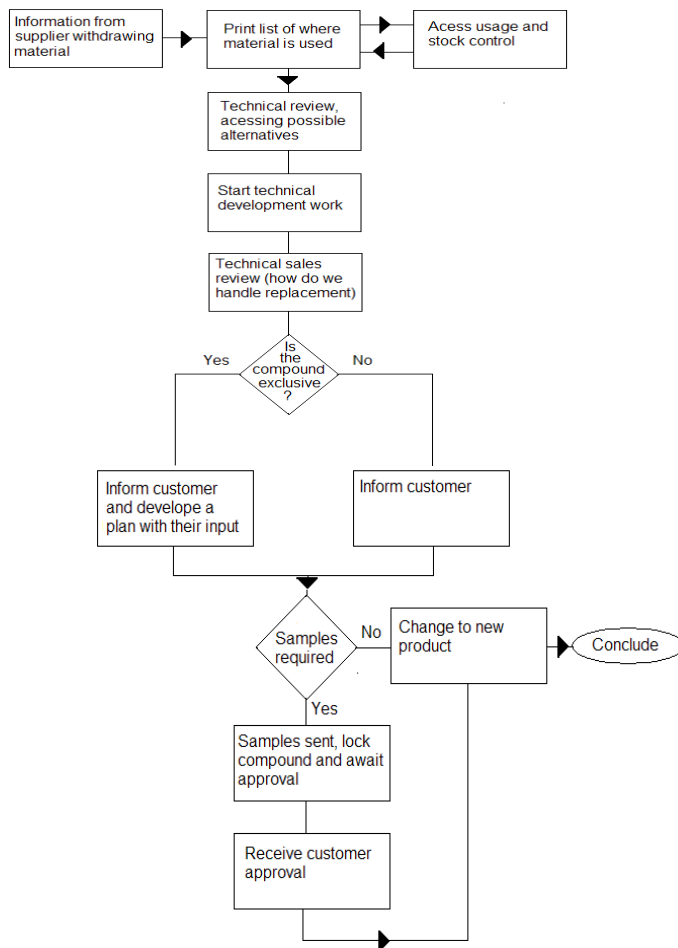
CONSEQUENCES OF CHANGE

As custom compounders it is difficult to know every customer's use for each of our compounds and their processing method for each part, and every synergy between one material and another. So even when there is a supplier's recommended replacement it is not always suitable. Also when there is a supplier replacement and internal evaluation it is often one of their own materials, as they don't want to lose sales. At Clwyd we try to evaluate what we feel are the best replacements in the whole market place independent of supplier.

Sevacarb MT formerly registered trademark of Columbian Chemicals Ltd

ISO 9001

The design element requirements within ISO 9001 prompted a change at Clwyd to concentrate efforts and resources in to looking at this area. The outcome has been a fully functional development database, this has also structured the way we handle change in our raw material supply. Now when changing materials whether it be forced or voluntarily there is a formal procedure. As stated earlier a raw material change if it were to be a common ingredient could affect many customers and hundreds of formulations each in a different way. Clwyd or its customers may have invested considerable money in testing and gaining external approvals for the compound, so we do try and restrict the number of changes when ever possible. An overview of this process can be shown schematically:



As noted earlier our preparation numbering system indicates exclusive compounds, in these instances the customer may wish to have an input into the development and may also take the opportunity to make more than one change whilst the compound may need re-approval.

CASE STUDIES

1. Replacement of ETU

Thiourea accelerators, particularly ETU were for many years the accelerator of choice. But with the ongoing emphasis on there possible toxicity, in 2004 we took a decision to cease the use of ETU as soon as we could find a suitable alternative. ETU when used with a secondary accelerator remains the best technical cure system, for a balance of cure rate, scorch and physical properties, such as modulus, resilience, and compression set resistance and provides excellent heat ageing properties. Over this period we have not been able to match the performance of ETU with a single material but have had to use a number depending on customer specification and production method. Current alternatives include:

HEXA, TMTD (Hexamethylene tetramine and tetramethyl thiuram disulfide): processing and bin stability are reasonable and physical results are comparable with ETU however compounds are deficient in heat ageing resistance. An unpleasant fishy odour is also noticeable.

HVA2, TMTD: good system that results in a good balance of heat resistance, scorch safety and compression set without the unpleasant smells, although requires a higher cure temperature.

MTT, HPCA (3-methyl-thiazolidine-thione-2, methyl-2-mercaptobenzimidazole): comparable physical properties and excellent heat age resistance, poor bin stability and most expensive of the alternatives.

Clwyd Development 10055

Evaluation of non ETU versions of BS 2752 C70

		HEXA	HVA	MTT	ETU
	Unit	Result	Result	Result	Result
Hardness	IRHD	73	74	72	74
Tensile strength	Mpa	15.1	15.8	17.6	16.8
E @ B	%	246	248	303	226
Mod @ 100%	Mpa	5.6	6	4.8	5.6

Compression Set					
24 Hrs @ 70°C	%	19	17	14	15

Heat Aged					
168 Hrs @ 70°C					
H. change		3	3	2	1
Tensile Change	%	-12	8	-1.7	1.8
E @ B change	%	-11	-3.2	-6.6	-4

Resistance to Liq B					
22Hrs @ 40°C	%	46	50	52	45

Low temperature					
5 Mins @ -30°C	Mpa	8.9	9.8	8.1	7

Rheology @		165°C	175°C	165°	165°C
Min		2.3	2.28	2.26	2.21
Max		19.44	18.33	20.77	21.88
T05		1.25	0.99	1.07	0.74
T50		3.44	4.38	4.96	2.95
T90		8.29	8.32	10.58	8.26

Storage stability

Mooney scorch @ 121°C after conditioning at 38°C					
		HEXA	HVA	MTT	ETU
Week 1	Mins/secs	20.49	>30	21.17	13.04
Week 2	Mins/secs	17.02	>30	16.31	12.42
Week 3	Mins/secs	12.46	>30	12.32	11.26
Week 4	Mins/secs	1.02	27.1	1.01	9.41
Week 5	Mins/secs	limit	25.51	limit	8.41
Week 6	Mins/secs		22.17		6.2
Week 7	Mins/secs		21.27		limit
Week 8	Mins/secs		18.48		

Mooney scorch @ 121°C after conditioning for 4 weeks @ 23°C					
		HEXA	HVA	MTT	ETU
	Mins/secs	15.51	>30	18.5	12.16

Each of these alternatives will meet BS2752 so are fair replacements although the only one to meet the full range of DTD5514 which has a more vigorous heat ageing requirement (168hrs@100°C) was the MTT.

Finally in July 2006 we were able to stop using ETU having satisfied our customers PCR requirements, although we haven't stopped researching alternatives or the effects of secondary systems. We would like to satisfy the need for a low temperature cure system with excellent bin stability.

2. Replacement of Dioctyl phthalate (DOP)

DOP is a widely used plasticiser within the polymer industry, predominately used in PVC and NBR. DOP offers a satisfactory all round performance and solubility at a low cost. There are many issues being raised within the plastics industry over its safety in plastic toys that have also brought into question its validity for use in compounds intended for repeated use in contact with food stuffs, as defined in CFR21, 177:2600. It's also a declarable ingredient within GADSL. On this basis Clwyd have actively been seeking a replacement, although no withdrawal timetable has been proposed. As with most other ingredients at Clwyd DOP goes into many hundreds of formulations to satisfy customers material requirements, both in-terms of specifications and processing.

The evaluation started by assessing 1,2-Cyclohexanedicarboxylic acid, diisononyl ester (DINCH) as a replacement, this looked satisfactory, although we encountered supply problems, so we have extended the evaluation to include diisononyl phthalate (DINP). Although this decision was made some months later due to the current development system it is easy to open these evaluations and keep consistency. Testing has been carried out on NBR, PCR and CSM to check solubility even at high levels. Low temperature properties were tested before and after heat ageing to evaluate the change in flexibility, this may be important for a part that is encountering heating and cooling cycles in service.

Clwyd Development 10040
DINCH versus DOP evaluation

	Unit	<u>PCR 15 phr plasticiser</u>			<u>CSM 15 phr plasticiser</u>		<u>NBR 10 phr plasticiser</u>		<u>NBR 30 phr plasticiser +15 phr Bisoflex 123</u>			<u>NBR 12 phr plasticiser to meet DTD 560</u>		<u>XNBR 15 phr plasticiser</u>	
		DOP	DINCH	DINP	DOP	DINCH	DOP	DINCH	DOP	DINCH	DINP	DOP	DINCH	DOP	DINCH
Hardness	IRHD	71	71	71	54	54	54	53	34	32	34	66	67	78	76
T.S	Mpa	8.9	9.1	8.6	16	15.8	11.4	11	5.2	5.1	4.95	12.9	12.1	18.8	19
E @ B	%	737	759	730	579	574	635	610	741	699	680	461	429	289	278
Mod @ 100%	Mpa	2.7	2.85	2.6	1.5	1.51	1.87	1.8	0.71	0.65	0.7	3.28	3.21	9.98	9.85

<u>Compression set</u>															
24Hrs @ 70°C	%	27	26	25	36	36	29	31	23	21	26	11	11	30	32

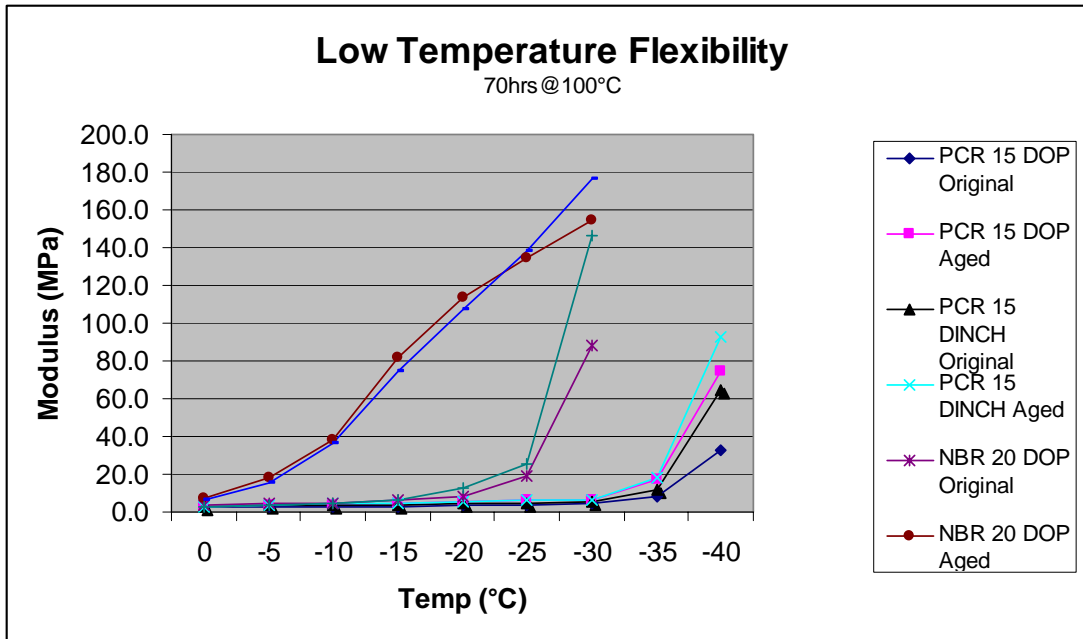
<u>Heat Aged</u>															
168Hrs @ 70°C															
Hardness change	IRHD	5	4	5	4	4	5	5	6	5	5	2	1	5	5
Tensile change	%	-2.2	-1	-4.6	5	10.7	-18	-9.1	-12.3	-12.0	-10.4	11.6	0.8	10.6	8
E @ B change	%	-5.6	-6.9	-2.1	-6.9	-5.7	-15.9	-10.3	-14	-7	-6	1	-4.2	-28	-32

<u>Fluid Resistance</u>															
70Hrs @ 70°C in ASTM 1															
Hardness change	IRHD	2	1	3	-2	-2	-2	-1	13	16	12	0	0	1	3
Volume change	%	-4.3	-4	-4	-3.4	-3.8	-4.2	-4.8	-18.2	-18.7	-18	-3	-2.3	-4.4	-4.2

<u>Heat aged</u>															
70Hrs @ 100°C															
Hardness change	IRHD	0	1	0	7	5	4	5	10	8	12	3	5	6	6
Tensile change	%	-15.7	-14	-11.6	-11.3	-2.5	-14.9	-12.6	-10.3	11	5	3.1	2	15.9	12.6
E @ B change	%	-6.9	-11.8	-6.2	-15.4	-13.5	-25	-24	-21	-19	-22.5	-18	-21	-38	-38
Wt loss	%	0.64	0.24	0.2	1	0.8	0.74	0.8	5.4	4.5	4.2	1.4	1.09	1.4	1.17

<u>Fluid Resistance</u>															
70Hrs @ 70°C in ASTM 3															
Hardness change	IRHD	-26	-23	-28	-23	-24	-7	-7	4	3	3	3	-1	1	1
Volume change	%	32.8	31.2	35	40	42	1.9	1.9	11.1	9.9	12.6	-1.3	-0.75	1.2	1.3

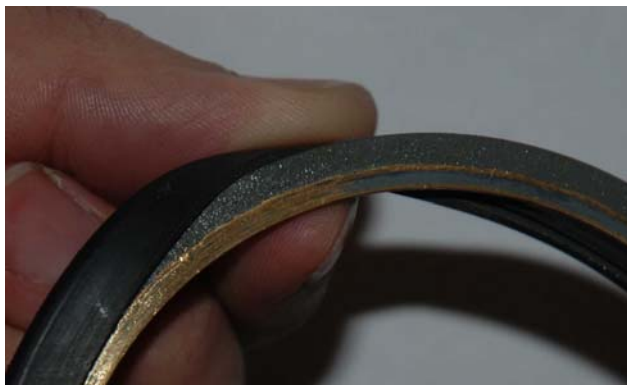
<u>Rheology</u>															
Tested at 165°C															
Min	dNM	1.02	1.01	0.92	0.56	0.55	0.44	0.44	0.13	0.13	0.14	1.08	1.36	0.99	0.95
Max	dNM	22.83	25.19	26.32	10.76	10.98	10.4	10.14	6.28	5.94	5.92	18.57	18.84	16.59	16.1
T5	mins	1.6	1.67	2.04	1.72	1.68	1.54	1.59	1.56	1.48	1.4	1.01	0.99	1.56	1.56
T50	mins	3.61	3.9	4.41	3.68	3.6	1.96	2.01	2.07	1.96	1.84	2	1.98	5.72	5.88
T90	mins	12.28	13.72	11.7	9.9	8.92	3.08	3.01	3.83	3.53	3.46	4.37	3.87	14.57	15.23



We also have had some specific bond testing and moulding carried out by one of our customers (see photos). As can be seen the moulding trials went well, the customer found a good match for shrinkage and improved flow when moulding the compound using DINCH. On moulding the bonded rings the DOP worked with just a primer where the DINCH failed to bond without using a top coat.



BK Boot
 5x5x3mm
 140secs @ 180°C
 64 cavities



DINCH with single coat



DINCH two coats

3. Replacement of Keltan 4802

Earlier this year Resin Express the then distributor for DSM gave us notice with regard to the withdrawal of Keltan 4802. Keltan 4802 is a high viscosity 52% ethylene medium ENB EPDM terpolymer. EPDM's can be heavily extended resulting in compounds with low percentage polymer content, despite this the polymer grade still has a large influence over the compounds physical properties and processing behaviour. Of the 190 active formulations using this polymer 85% of them also contain another polymer as a blend, this has a two fold affect. Firstly as a blend you are not matching the whole polymer content so for example at 50% the error is reduced by half although the reason for a polymer blend is often to improve processing so it is more specific to the customer and their process.

Clwyd Development 10087
EPDM evaluation (replacement of Keltan 4802)

Polymer Type		Keltan™ 4802	Kep 270	Nordel™ 4570	Keltan™ 8340A
	Unit	Result	Result	Result	Result
Hardness	Shore A	72	74	74	73
Tensile strength	Mpa	15	13.2	15.1	15.2
E @ B	%	317	353	320	313
Mod @100	Mpa	4.6	3.7	4.7	4.7
Tear	N/mm	36	32	33	36

Compression Set					
22 Hrs @ 70°C	%	9.2	10.5	7	9

Heat Aged					
168 Hrs @ 70°C					
H. change		0	0	1	4
Tensile Change	%	-1.3	1	-4.6	1.3
E @ B change	%	-5	-12	-10.9	-8.9

Low temperature					
5 Mins @ - 40°C	Mpa	6.83	5.25	15.6	7.46

Resistance to Ozone					
72Hrs @ 40°C 25 pphm	Pass/Fail	pass	pass	pass	pass

Wallace Plasticity					
		46	51	55	60

Polymer Viscosity 1+4 @ 100°C					
		99.3	85.6	91	92
Ethylene	%	52	52	50	55
Diene	%	4.5	4.5	4.9	5.5

Rheology @ 165°C		Keltan 4802	Kep 270	Nordel 4570	Keltan 8340A
Min		2.61	2.22	2.62	2.65
Max		22.09	21.17	28.11	25.9
T05		1.09	1.07	1.08	1.06
T50		2.74	2.49	2.66	2.83
T90		10.78	7.22	12.94	13.48

It must also be noted; the Keltan™ replacement has too high a third monomer content (enables sulphur cross-linking) to be used in FDA applications, the limit being 5%.

Conclusion

Changes in legislation and the withdrawal of raw materials are inevitable. The paper demonstrates that with careful planning and sensible timing the trauma caused by such events can be minimised. In some cases the results lead to an overall improvement in technology giving benefits to the compounder and moulder alike. As somebody once said every problem is an opportunity.

Acknowledgements

Like to thank Andrew Piper of DP Seals for their help in providing moulded samples and the laboratory staff at Clwyd for generating data.