Cutting Emissions and Energy While Improving Performance With Next-Generation Engine Filter Media

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Abstract

The engine filter media industry is undergoing dramatic change. Traditional phenolic-treated media must be reformulated to meet three challenges posed by engine filter manufacturers: Customers want media with increased strength and longer service life in final cured form, they need to use less energy in curing processes, and they demand greater reductions in media emissions from formaldehyde, phenol, and phenolic condensate by-products.

To meet these demands, media producers have undertaken concerted efforts to develop next-generation, higher-performance, pre-cured resin systems. These new materials offer improved physical strength of up to 20%, increased resistance to thermo-oxidative aging, and increased flexibility. At the same time, they cure more quickly, significantly reducing energy demands in processing the final product.

Finally, this report shows how, using the latest phenolic-based advanced cure resin (ACR™) technology, the level of emissions given off during media assembly can be reduced significantly compared with traditional resol-based phenolic resins.

Introduction

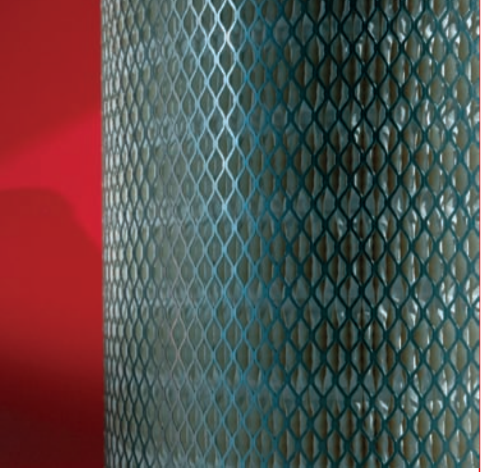
The European market demands an even higher level of engine filtration performance than the U.S., due to longer service intervals than the U.S norm. Vehicle service intervals of 20,000 to 30,000 miles are not unusual in Europe, given the mileage reached between annual servicings. Recently, companies such as Renault have introduced 2-year service intervals, requiring media with even higher physical strength in aggressive synthetic lube and higher-temperature air and lube applications.

Thermoplastic resins are widely used in certain applications, such as gas turbine and heavy duty air. However, European performance demands usually favor the use of thermoset phenolic or melamine resin technologies for lube and environments that require water, chemical, and temperature resistance.

The challenge of emissions

Historically, filter elements were constructed from paper impregnated with uncured (A-staged) phenolic resins and dried to a constant moisture level. These media are slow-curing and emit — as "blue smoke" — high levels of phenol, formaldehyde, ammonia, and residual solvent during the filter element manufacturing process. This necessitates the use of energy- and capital-intensive emissions control systems such as thermal oxidizers, as well as high levels of ventilation.

(Note that new high-performance acrylic thermoset resins have zero emissions, but remain considerably more expensive than solvent-based phenolic resins. Media made from these materials have not been widely adopted by engine filter makers.)



Control of emissions into both working and external environments has become much more stringently regulated, with tightening of regulations on occupational exposure limits (OEL) for phenol and formaldehyde. (See Table 1 below.) While phenol is a known toxic substance with a U.K. maximum OEL of 2 ppm (8 hr), recent concern has focused on formaldehyde — classified by the 11th Report on Carcinogens as "reasonably anticipated to be a human carcinogen" and by IARC as “carcinogenic to humans (Class 1).” Formaldehyde emissions have been tightened in France, and banned outright in some applications in the EU as a whole. Labeling requirements for media emitting over 1000 ppm plus emissions controls are now in place in the U.S.

Table 1: Formaldehyde hazard classification for selected industries

Country	Hazard Class(es)	Symbol(s)	Label	Limits ppm				Comments & Specific Issues (+)
				TWA	STEL	Ceiling Value	OELs	
EU	T, C, C3 C1 or C2(**)	C, T, Xn, Xi	R34,40,43; 20/21/22; 23/24/25; 36/37/38					EU issues guidance limits only. Regulations are set within the member countries.
France	As EU + C1 (**)	As EU	As EU		1		0.5	Law changed 13th July 2006 (*): Exposure limit reduced to C1 levels from January 2007
Germany	T, C, C1(+)	As EU	As EU			0.3		BfR: C1 BfR: Indoor Air Quality (Max Concentration: 0.1 ppm)
United Kingdom	As EU	As EU	As EU	2	2			
China	C, T	C, T	5.6, 5.22, 5.48, 5.94, 5.99, 5.103, 5.111, 5.117		2			
Japan	attached	C, T		0.5				C2
U.S.	C, T, C1/2	C, T		0.75	2	0.5		Including California

Key

TWA	Time-weighted average (TWA) concentration
STEL	Short-term exposure limit
Ceiling value in	Ceiling value is the maximum permissible concentration of a hazardous material the working environment
OEL	Occupation exposure limit (over 8 hours)
C	Corrosive
Cx	Carcinogen category = X
Car. group IIIB	Carcinogens group: IIIB (Justifiably suspected of carcinogenic potential)
T	Toxic
Xi	Irritant
Xn	Harmful
R34	Causes burns
R40	Limited evidence of a carcinogenic effect
R43	May cause sensitization by skin contact
R20/21/22	Harmful by inhalation, in contact with skin, and if swallowed
R23/24/25	Toxic by inhalation, in contact with skin, and if swallowed
R36/37/38	Irritating to eyes, respiratory system, and skin

With these increases in both energy and environmental costs of ownership, filter element manufacturers now look to alternative material technologies to deliver a cost advantage in the final product.

Advanced cure resin technology

A new generation of cleaner, higher-performance, flexible phenolic resin technologies has recently arrived in both the U.S. and Europe. These materials significantly reduce energy demand through higher cure speed, and cut emissions into the environment during manufacture. Combined with modern manufacturing processes, they have a potentially lower environmental impact than current water-based technologies.

Advanced cure resin (ACR) technologies comprise phenolic-based filter media where a predefined additional level of cure is applied to the resin during the manufacturing process. ACR materials can be supplied in ranges of pre-cure from 30% to 100%, depending on the ability of the customer to handle materials that are significantly more springy than traditional B-staged phenolic resins. This pre-curing by the supplier results in reduced curing energy or in faster curing at existing oven temperatures.

Faster curing

Reduced curing times can be further enhanced through the use of fast-cure resin formulations. When the degree of cure is tracked by acetone extraction, testers see a significant improvement in the cure speed of the latest European resins compared with the traditional resol-based approach.

Pre-cured resins — in combination with modern formulation design — offer the customer a significant improvement in process economics over traditional phenolic-based media. Where circumstances such as pleat processability permit, they can even remove the need for curing ovens.

Improved performance

Advanced cure resins also show higher levels of physical strength and performance in comparison with traditional phenolic resin technologies. ACR media exhibit:

- Tensile and burst strength up to 20% higher (depending upon the permeability of the base paper)
- Aged tensile strength (24 hours at 160°C) significantly higher than with standard phenolic resins, allowing lower resin content to be used (see Figure 1)
- Higher levels of flexibility compared with traditional phenolic resols when highly cured
- Higher levels of inherent stiffness, enabling higher pleating speeds with greater pleating heights, plus reduced fiber and dust buildup on heated portions of pleaters
- Reduced reel tracking issues with higher manufacturing consistency (manufacturing to a degree of cure and not just dryness), since the media is more consistent in both machine and cross directions
- Faster curing resins (up to 40% faster curing) with lower energy requirements for element curing (see Figure 2)

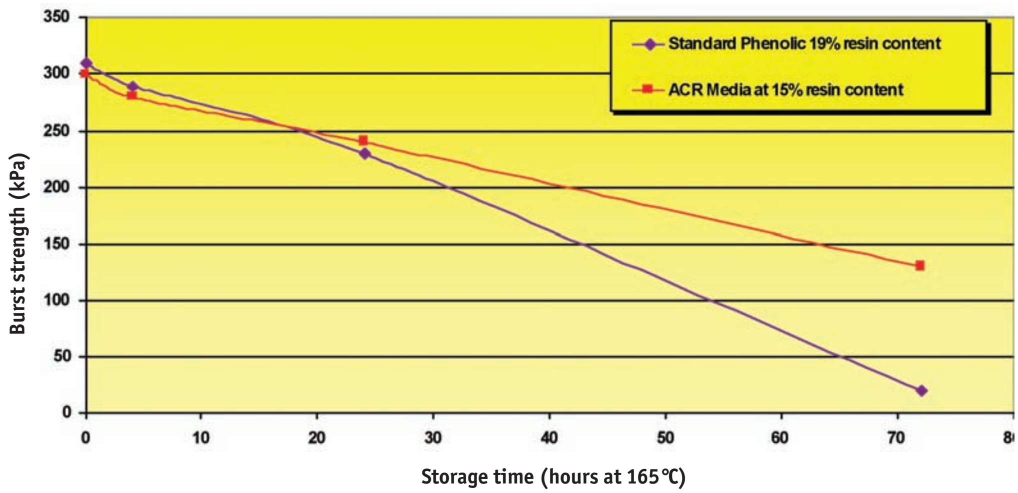


Figure 1: Thermal aging characteristics of advanced cure resins versus standard cure phenolic resins

(Extended aging at 165°C)

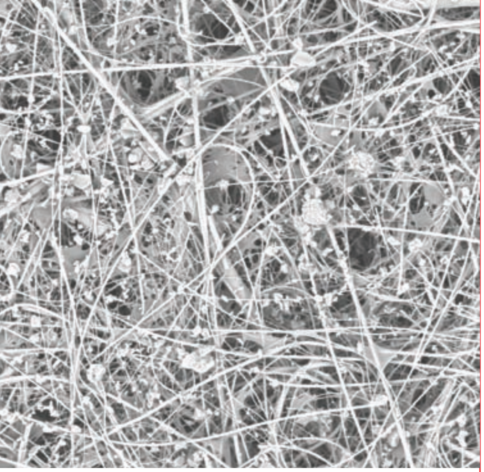
Reducing emissions

Emissions from media impregnated with phenolic resin are well documented. Traditional phenolic resins emit relatively high levels of free monomers during preheating and post-curing. In some countries, this mandates the use of emissions control systems such as ventilation and thermal oxidation. During curing, the traditional phenolic "blue smoke" is limited to phenol, formaldehyde, ammonia, and water up to 250°C.

Much work in emissions reduction has focused on the systematic reduction of phenol and formaldehyde. Phenolic resins in Europe typically have resols with specified free phenol of <1.5% and novolacs with free phenol of <0.5%, while formaldehyde levels are low enough to remain unspecified. In the U.S., for a resol typical levels of free phenol and formaldehyde remain significantly higher. Levels of <5.0% free phenol and <1.0% free formaldehyde are specified by all major manufacturers.

While cleaning up phenolic resins has significantly reduced the level of free phenol in standard B-staged examples, the level of emissions into the atmosphere remains high. Pre-curing offers a clear future benefit.

Hollingsworth & Vose Company, a leading producer of filter media, recently undertook a study to determine actual reductions in the levels of free phenol and formaldehyde that might be achieved with ACR materials.



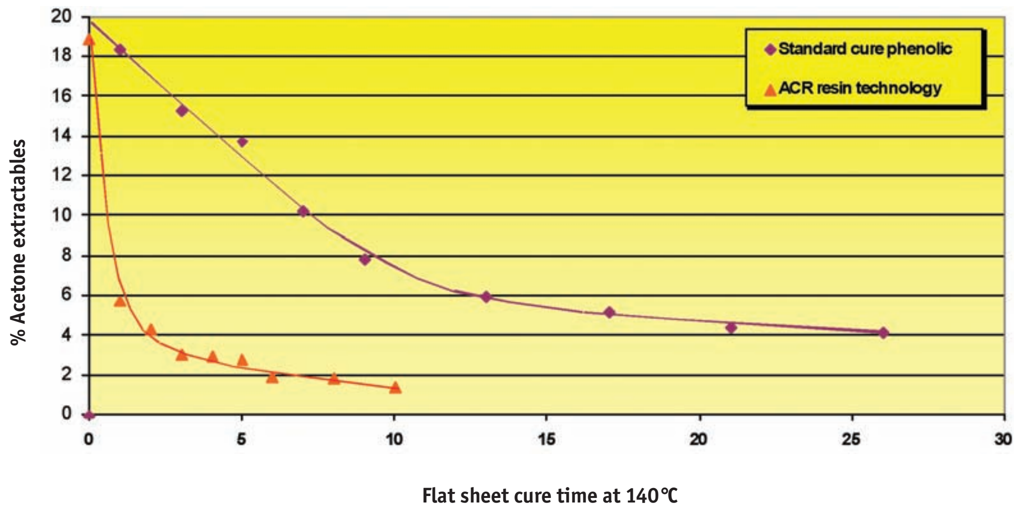


Figure 2:
Cure profile of advanced cure resin technology in comparison to standard cure phenolic resins
Cellulose base paper with 20% resin content

Testing emissions two ways

This study examined the evolution of free phenol and formaldehyde from a commercial European advanced cure phenolic product, versus a comparable traditional, standard cure phenolic resin commonly found in the European market. All tests were carried out by INFRA-SERV Knapsack, an independent test laboratory, using a minimum of five samples per test.

In the study, A4 handsheets of a standard cellulose panel air media were impregnated with two standard resin formulations and air-dried at room temperature. This provided a baseline of 0% pre-cured media.

Samples were pre-cured to different degrees of cure using a Mathis LTE lab dryer at 140°C and 2000 rpm to achieve approximately 60% and 90% pre-cure. (These percentages were measured by a standard 85/15 acetone/methanol extraction testing protocol, where full extraction is assumed to be no-cure and 0% extraction is assumed to be 100% cure.)

Test protocols

Tested levels of free phenol and formaldehyde found in any media are dependent upon the nature of the test protocol. For this study, researchers implemented two protocols:

- **VDA275:** A sample of the filter media was hung from the lid of a sealed jar above a fixed volume of water, placed in an oven at 60°C for 3 hours, then extracted and treated with a fixed amount of acetyl acetone and ammonium acetate. The level of formaldehyde was determined by colorimetry against a precalibrated chart. This analysis, the accepted standard test for formaldehyde in Europe, is accurate to around 100 ppm.
- **Off-gassing:** Working in conjunction with the external testing laboratory, Hollingsworth and Vose researchers developed an off-gassing test protocol to determine the emissions levels of phenol, formaldehyde, and ammonia expected from media during an average cure cycle in a typical production environment. Samples were heated for 15 minutes at 158°C under a nitrogen flow of 1 L/min. to ensure complete cure and liberation of free

volatile materials. A DNPH tube was placed behind the oven to absorb off-gassing residues. After 15 minutes, the sample was removed, and nitrogen was passed through the empty oven for a further 15 minutes at the same temperature. The DNPH tube was then removed, and levels of phenol and formaldehyde in the elute determined by HPLC.

Results: formaldehyde levels

Extraction testing showed two significantly different levels of free formaldehyde — differing by at least a factor of 10. The VDA test (and also the comparable AATCC test protocol) showed emission of significantly higher levels of free formaldehyde than the off-gassing technique (see Figure 3 below).

These differences in the mass balance are suggestive. They demonstrate a clear if not precisely defined link between the two test protocols over a wide range of formaldehyde emissions (Figure 4). The factorial difference increases significantly at very high levels of free formaldehyde; the relationship is nonlinear.

The best explanation comes from the conditions at which each technique operates. The off-gassing technique attempts to simulate real-world conditions. It may better replicate a realistic production curing environment, where at 158°C the free formaldehyde is available to undergo curing as well as to be released into the environment. By contrast, the VDA test methodology measures the total amount of free formaldehyde that can be released into the environment at a significantly lower temperature of 60°C — a temperature at which no competing chemical reaction can occur.

Both sets of results (see Figure 3 on cured and uncured samples, and Table 2 on partially pre-cured samples) show a marked reduction of free formaldehyde levels in the ACR product versus the standard cure phenolic resin technology, especially at low levels of cure. Note: in the VDA tests, the detection limit of 100 ppm was a barrier to accurate measurement of the total level of formaldehyde.

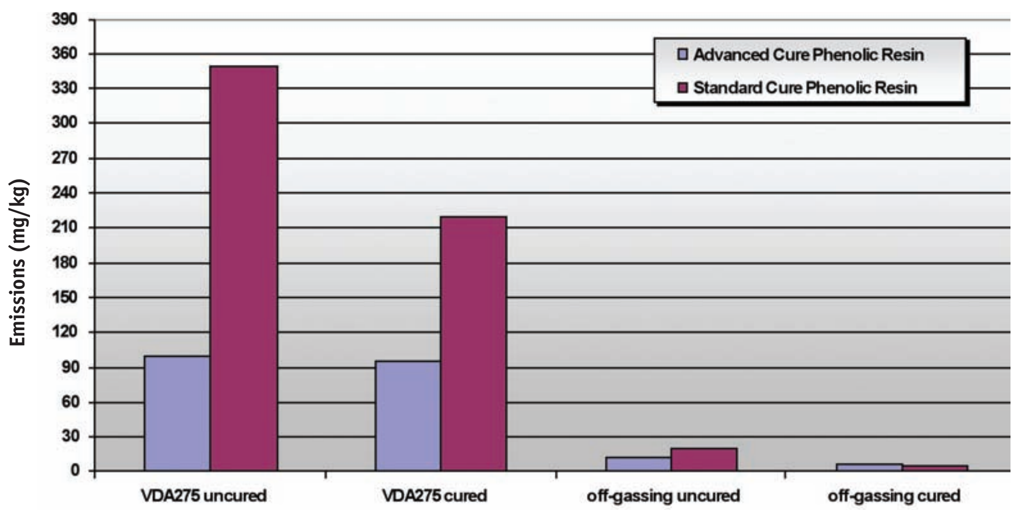


Figure 3: Formaldehyde emissions from cured and uncured phenolic resins by VDA275 and off- gassing studies

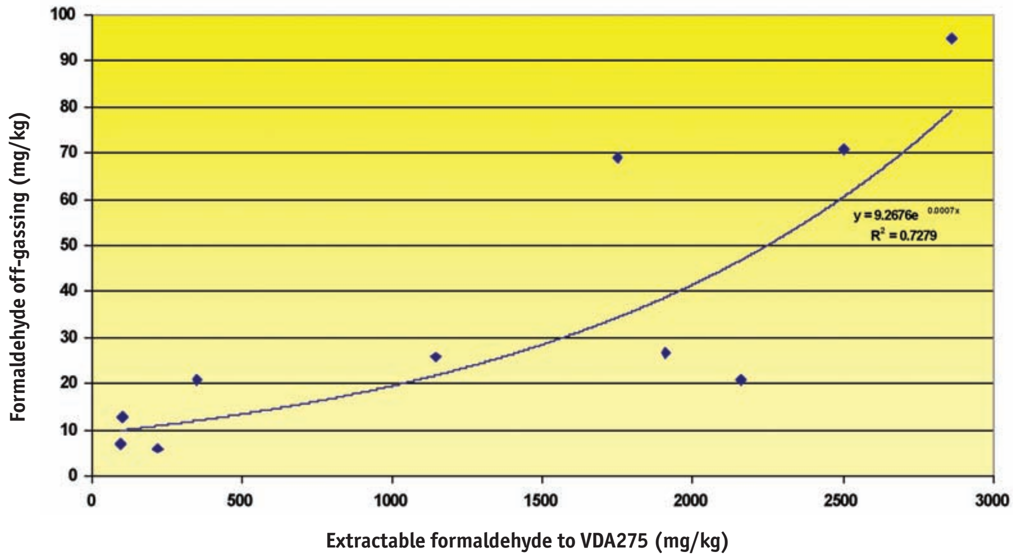


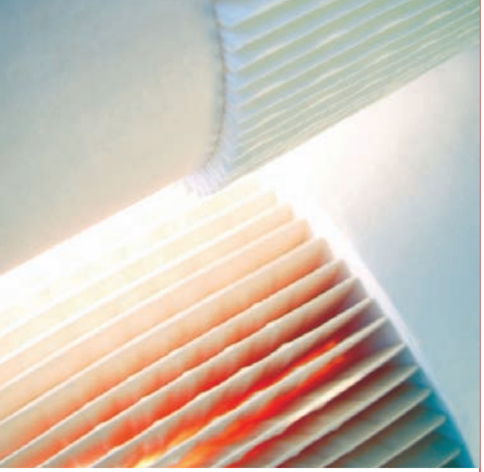
Figure 4:
Off -gassing emissions versus extractable formaldehyde to VDA275 for a range of materials

Compared to melamine-based resin technologies, phenolic resins lack ability to generate additional formaldehyde with additional heating. Consequently, testing shows a reduction in emissions with increasing pre-cure for standard cure phenolic media (Figure 5), with a strong exponential decay.

Table 2:
Results of pre-cure studies on standard cure and advanced cure phenolic media

	Standard cure phenolic resins		**Advanced cure phenolic resins**	
VDA275	Formaldehyde by VDA275 (mg/kg media)	Phenol by off-gassing (mg/kg media)	Formaldehyde by VDA275 (mg/kg media)	Phenol by off-gassing (mg/kg media)
Degree of resin pre-cure (by acetone extractables)				
0%	338	34.6	113	11.5
60%	192	25.7	175	20
90%	163	20.8	102	19.7

ACR media exhibit very low initial levels of free formaldehyde, close to the detection threshold of the VDA test protocol. These media thus show no perceptible drop in formaldehyde emissions with curing.



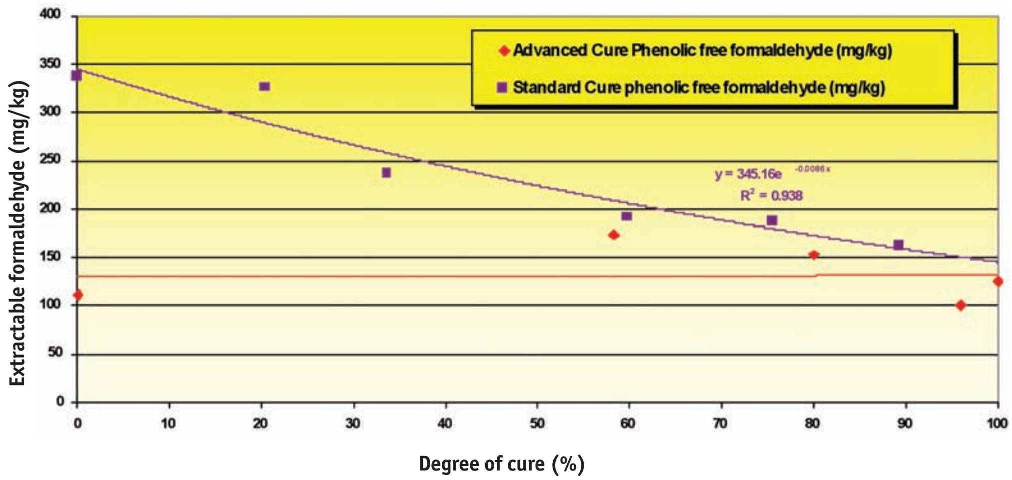


Figure 5: Reductions in free formaldehyde as a function of cure for advanced cure and standard cure phenolic systems

Results: phenol levels

The levels of free phenol and ammonia in the ACR media could only be determined by off-gassing. However, the boiling point of phenol (181°C) precludes the emission of 100% of the free phenol into the environment during a typical curing cycle at 160°C. As with formaldehyde, the absolute amount of phenol that can be emitted into the atmosphere is strictly limited; an acetone extraction test in conjunction with HPLC would almost certainly give a higher level of extractable material. Research into this question is ongoing. Certainly levels of off-gassed phenol and ammonia emissions associated with ACR material are lower than with standard cure phenolic resins (Table 2). Again, results were limited by the accuracy of the test to detect free phenol (10 ppm) and tended to show a maximum rather than a decrease with level of cure.

This study showed a relatively strong correlation between phenol off-gassing and formaldehyde extraction (Figure 6), with a linear relationship between the two techniques.

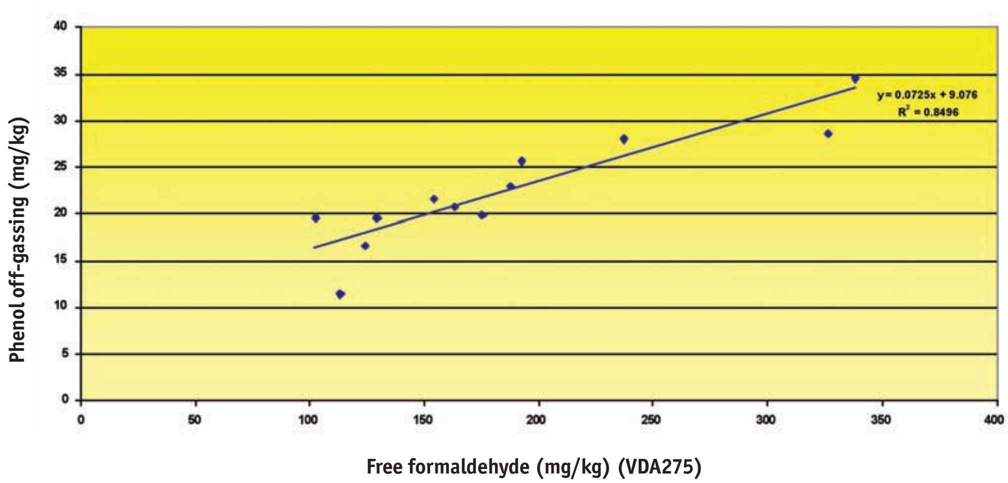


Figure 6: Correlation between phenol off-gassing and free formaldehyde for all resins

Emissions studies always ignore the ability of low-molecular-weight, polycondensate by-product materials (notably methyloyl functionalized phenol) to be off-gassed into the environment. These materials are of concern because they can create deposits in air handling system ductwork, necessitating additional maintenance. Emission of these materials is governed by the level of free monomers present in the initial resin. ACR formulations that reduce free monomer levels should have a positive impact on these concerns.

Summary: significant ACR advantages

Innovative ACR technology offers significant performance advantages over traditional phenolic resin systems in air, lube, and fuel filtration.

As pioneered by leading materials manufacturer Hollingsworth & Vose, these phenolic-based, advanced cure resins demonstrate greater flexibility, strength, and age resistance. H&V's latest ACR technology offers the end user a range of design options, including:

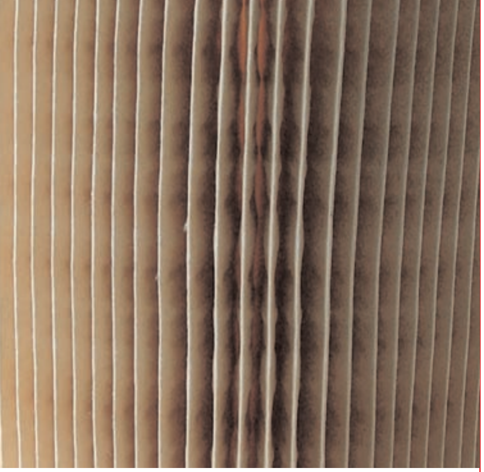
- Reduced resin content for the same level of strength and physical properties
- Increased aged strength for longer life
- Reduced levels of scrap waste
- Lower energy demands
- Higher throughput

(ACR technology does require appropriate processing handling, to deal with inherent springiness imparted by the higher molecular weight of the resin.)

This technology also provides some answers for rising concerns about emissions from the manufacture and processing of filter elements. A recent study examining emissions from advanced cure phenolic resins compared with standard cure phenolic resins shows that ACR materials offer significant environmental benefits to the end user, through reduced phenol and formaldehyde emissions on partially pre-cured and fully cured media. Contributing to these reduced emissions are two factors:

- Cleaner resins being developed in Europe
- Partial or full pre-curing, enabling the end user to realize significant reductions in levels of emissions into filter assembly lines and into the environment

The study also suggested a possible relationship between testing protocol conditions and measurable free phenol and formaldehyde. This observation raises questions about whether customary testing methods accurately represent the actual level of material liberated during processing. Further work is proceeding within the industry on these questions.



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About H&V

Established in 1843, Hollingsworth & Vose Company is a global leader in developing, manufacturing, and supplying technically advanced engine, high efficiency, and liquid filtration media; battery materials; and industrial nonwovens. H&V adds value to customers' products by inventing next-generation materials with superior performance. H&V's expertise and process capabilities include wet-laid, dry-laid, meltblown, nanofiber, and composite technologies. The company operates manufacturing sites and research centers in the Americas, Europe, and Asia.

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