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Chemical and Functional Responses to Brake Lining Cure Variations

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ABSTRACT

A study was made of the responses of pyrolytic gas chromatography (PGC) and the friction assessment screening test (FAST) to variations in curing conditions for a liquid, oil-modified, phenolic resin system. Both PGC, which characterizes the organic resin, and FAST, which characterizes the friction and wear properties, show systematic variations with changes in cure time and temperature. A linear relationship exists between the area of one PGC peak (phenol) and the wear as determined by the FAST procedure.

A chemical kinetic model is postulated which relates the concentration of phenol produced on pyrolysis to a function of cure time and temperature. An index of cure is introduced which defines the curing conditions in terms of a single parameter. The PGC phenol peak area, FAST friction, and FAST wear correlate well with this index of cure.

FORD MOTOR CO. RELIES upon several test procedures to assure consistency of the friction materials used on its vehicles. Among these procedures are pyrolytic gas chromatography (PGC), a test to characterize the organic constituents of the friction material, and the friction assessment screening test (FAST), a test which characterizes the friction and wear behavior of the material. Detailed descriptions of these tests and illustrations of their efficacy have been published previously. (1, 2)*

In addition to their usefulness as quality assurance tests, these procedures can serve as valuable tools for laboratory studies of more fundamental phenomena in friction materials. The sensitivity of both tests to material compositional variations has been shown previously. It has been found that these tests are also sensitive to certain processing variables such as cure time, cure temperature, and cure agent concentration. This paper describes a study of friction material curing conditions for a typical liquid, oil-modified, phenolic resin system and the relationship of the PGC and FAST responses to changes of cure.

*Numbers in parentheses designate References at end of paper.

SAMPLE DESCRIPTION

The response of PGC and FAST to variations in cure conditions was studied using two groups of samples. The first group of samples was used to study cure time and temperature variations. The second was used to study variations of the cure agent concentration at selected times and temperatures.

The first group contained a single set of samples from the same wet mix. This model brake lining system consisted of asbestos, an oil-modified, phenolic liquid resin (a typical brake lining resin), hexamethylenetetramine (hexa) cure agent, and barium sulfate. The samples were cured at four different temperatures, nominally 250, 300, 350, and 400 F, for cure times of 1, 2, 4, 8, and 16 hr at each cure temperature. The hexa concentration recommended by the manufacturer -- 15% of the "solids" content in the resin -- was used in this group of samples.

The second group of samples consisted of three sets of samples with variations in the cure agent concentration. These mixes had compositions identical to the previous group, except that the hexa concentration was varied from mix to mix. Hexa concentrations of 10, 15, and 20% of the

resin "solids" were used for this study. The samples were cured at four different temperatures (250, 300, 350, and 400 F) for cure times of 1-1/3, 2-2/3 and 4 hr at each cure temperature. The effect of cure agent concentration on cure was expected to be more predominant at early cure times; therefore, cure times beyond 4 hr were not investigated.

TEST PROCEDURE

PYROLYTIC GAS CHROMATOGRAPHY - The PGC test involves the pyrolysis of a sample followed by the instrumental separation and the sensing of the products of decomposition. When the pyrolysis conditions are kept constant, the products of decomposition can be used to characterize the organic constituents in the original material. A schematic diagram of the pyrolytic gas chromatograph is shown in Fig. 1.

A small solid sample is inserted in the loop formed by the platinum-rhodium ribbon at the tip of the pyrolysis probe. Current is applied to the probe tip, causing the tip to become heated to a high temperature, thereby pyrolyzing the organic material in the sample. The products of pyrolysis are swept by a stream of helium into the chromatographic column. The column separates the pyrolysis products, allowing the individual components to elute from the column at different times. The presence of an organic component in the exit stream is sensed by a flame ionization detector, the output of which is recorded with time as a series of peaks. Each peak corresponds to a particular decomposition product, while the area under the peak corresponds to the quantity of that product.

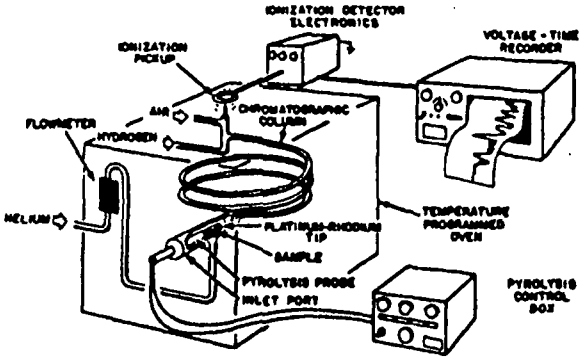

Fig. 1 - Schematic diagram of gas chromatograph

The test conditions used are those specified by Ford for quality assurance of brake linings. A more detailed description of the equipment and test procedure is given in the literature. (1)

FAST - The FAST machine provides a convenient laboratory method for characterizing the friction and wear behavior of friction material. Test procedures for this machine in a constant output (that is, constant friction force) mode of operation are particularly well suited for quality control of brake lining materials. The machine provides highly reproducible results which correlate well with vehicle performance.

The FAST machine with its associated recording instrumentation is shown in Fig. 2, and a schematic diagram of the test geometry and load control system is shown in Fig. 3.

As shown in the schematic diagram, the sample clamping load is applied by hydraulic pressure acting on a rolling diaphragm load cell. The friction force is transmitted directly to the friction valve spool. In the constant output mode of operation, any variation of the friction force from equilibrium results in a displacement of the clamping valve spool. This causes the clamping pressure to increase or decrease, so as to provide the friction force that re-establishes the original equilibrium. In this manner the control system maintains the friction force constant within 0.1 lb through modulation of the clamping load. The magnitude of the friction force is selected by means of the load control screw.

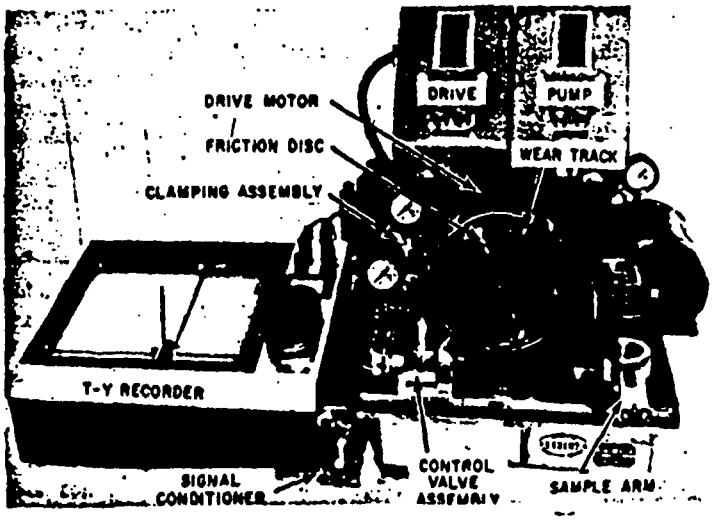

Fig. 2 - FAST machine with auxiliary instrumentation

The test procedure used for this study is the one Ford specifies for the quality assurance of brake linings. This procedure calls for a flat 1/2 in. square sample to be dragged for 90 minutes against a cast iron test disc at a surface velocity of 23 fps, while maintaining a friction load of 17.4 lb at the sample. The cast iron test disc reaches a temperature of 560 F during the test because of the heat generated at the friction interface. Since the rate of power dissipation is held constant, the history of temperature versus time and the total work done is the same in all tests; therefore, wear results (total sample weight loss) can be compared directly.

A complete description of the FAST machine and details of its sensitivity and reproducibility can be found in the literature. (2)

RESPONSE OF PGC TO CURE CONDITION VARIATIONS

CURE TIME AND TEMPERATURE EFFECTS - The effect of cure temperature on the chromatograms is illustrated in Fig. 4. The chromatograms shown are those of samples cured for 16 hr at the four different temperatures (250, 287*, 350, 400 F). As the cure temperature is increased, the area of peak A increases, while the area of peak C decreases.** Numerous other peaks show either an increase or decrease in area as the cure temperature is varied; however, the magnitude of their changes is less than that for peaks A and C. Even though peak B is a major peak, the peak area is less sensitive to changes in cure time and temperature.

The area of peak C plotted against cure time with temperature as a parameter is shown in Fig. 5. This peak shows a systematic decrease in peak area as cure time is increased. Fig. 6 is a plot of the area of peak A versus cure time with temperature as a parameter. The solid lines in this figure represent the expected values based on a chemical kinetic model, which will be discussed in a later section. The points indicate the experimental values. The data show a systematic increase of peak area with increasing cure time for each cure temperature, except at the initial portion of the 250 F cure, where initiation of cure is believed to have been mar-

*The nominal 300 F was actually 287 F.

**The peak area percentage is obtained by a normalization procedure. For this resin system, 21 peaks with a reasonably large response were selected and their peak areas measured. Then the percent area of a particular peak is equal to its area divided by the sum of the 21 peak areas.

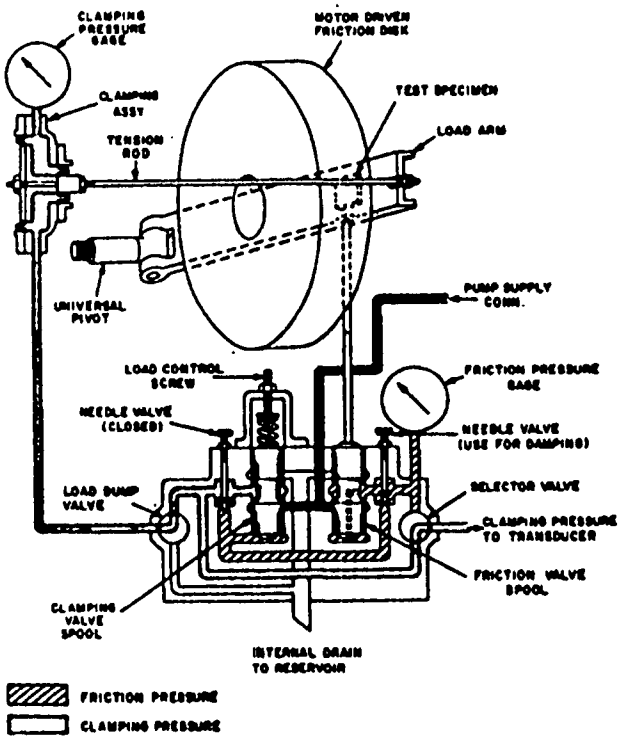

Fig. 3 - Schematic diagram of test geometry and load control system

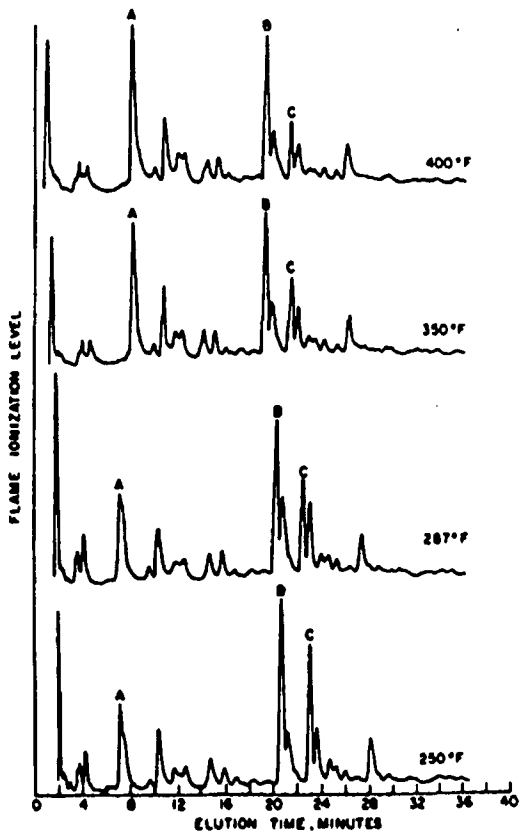

Fig. 4 - Effect of variation of cure temperature on PGC --- cure time 16 hr

ginal. This somewhat erratic behavior for the 250 F curve is attributed to additional curing of the samples in the injection port of the chromatograph.

Because the area of peak A is used in the construction of the chemical kinetic model, the major decomposition product corresponding to peak A was trapped and identified as phenol. Numerous techniques for chromatographic peak identification are well defined in the literature. (3) In this case, the outlet gas stream just before peak A emerged was passed through a U-shaped capillary tube submerged in liquid nitrogen. The condensed sample (in the capillary) then was identified as phenol by ultraviolet absorption techniques.

For this particular resin system, it is apparent that the PGC is extremely sensitive to changes in cure temperature; however, it was found to be sensitive to cure time only in the early stages of cure. As shown in Fig. 6, the curves tend to level off beyond a 4 hr cure.

CURE AGENT CONCENTRATION EFFECTS - To describe qualitatively the influence of cure agent concentration on the PGC response, only the extremes in hexa level will be discussed (10% and 20% of resin solids). Generally, the PGC response to the 20% hexa samples was similar to the 15% hexa samples. This indicates that 15% hexa is adequate to achieve sufficient cure. In addition, the PGC response to the 15% hexa samples in this group of samples was consistent with the results described in the previous section.

Fig. 7 shows chromatograms of samples which received a 1-1/3 hr cure at 300 F for the high (20%) and low (10%) percentage of hexa. The top chromatogram results from the pyrolysis of hexa alone. The high hexa chromatogram shows a small shoulder on the leading edge of peak D (arrow), which corresponds to the major peak of pyrolyzed hexa. The shoulder is evident in the high hexa chromatograms for all curing conditions tested. It does not appear in the particular chromatogram shown in Fig. 7 for low hexa, but it does appear in other low and normal (15%) hexa chromatograms. The random occurrence of this shoulder in the latter chromatograms is attributed to local variations in the distribution of hexa within the samples.

The variation of the PGC results with hexa concentration is not yet understood. A change in the hexa concentration did not produce a systematic variation in the area of any of the PGC peaks, as was observed with cure time and temperature variations. In fact, the low and high hexa samples showed a reversal in the area of peak A as the temperature is increased. That is, for cure temperatures of 250 and 300 F and cure times of 1-1/3, 2-2/3, and 4 hr, the areas of peak A for the 10% hexa samples generally were lower than the 20% hexa samples. At cure temperatures of 350 and 400 F, the area of peak A generally was higher for the 10% hexa samples; this behavior suggests a complex cure mechanism.

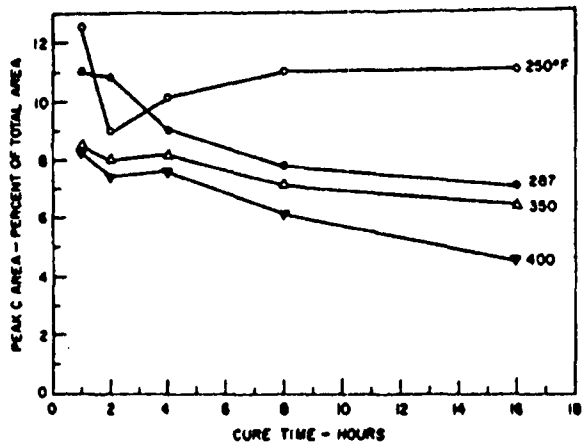

Fig. 5 - Variations in area of Peak C with cure conditions

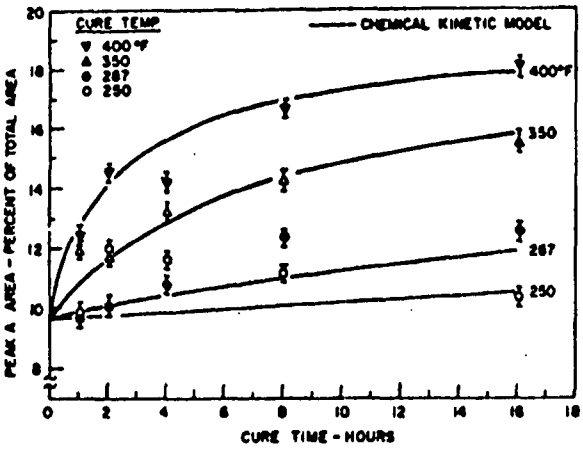

Fig. 6 - Variations in area of Peak A with cure conditions

CHEMICAL KINETIC MODEL OF RESIN CURE

A chemical kinetic model is postulated which relates the area of peak A (phenol) to the cure time and tempera-

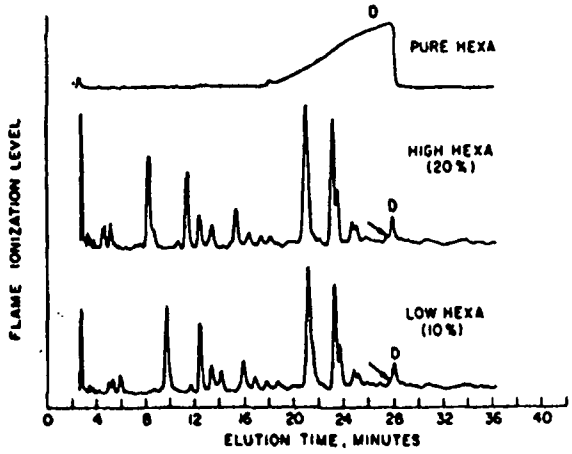

Fig. 7 - Effect of variation in hexa concentration on PGC

ture. (4) The model is constructed by relating the rate of formation of crosslinked structure (x) to the concentration of noncrosslinked precursors (y). It is further hypothesized that phenol is a measure of the crosslinked structure. The interrelationships between the precursors, crosslinked structure, and cure conditions can be expressed mathematically by the following equations:

Concentration of precursors at any instant:

$$y = y_0 - cx \tag{1}$$

Chemical rate equation:

$$-\frac{dy}{dt} = c\frac{dx}{dt} = ky^n \tag{2}$$

Arrhenius equation:

$$k = k_0 e^{-E/RT} \tag{3}$$

Relates peak area to concentration:

$$x = PA \tag{4}$$

where:

- y = Concentration of noncrosslinked precursors to x
- x = Concentration of crosslinked structure -- phenol is a measure of x
- n = Order of reaction
- k = Chemical kinetic rate constant
- k_0 = Arrhenius constant
- E = Activation energy
- c = Constant
- y_0 = Initial Concentration of y
- A = Relative area of phenol peak
- P = Constant for this resin system when tested using same apparatus and test procedure
- R = Universal gas constant
- t = Cure time
- T = Cure temperature

Combining Eqs. 1-4 gives the following differential equation:

$$c\frac{d(PA)}{dt} = k_0 e^{-E/RT}(y_0 - cPA)^n . \tag{5}$$

If $n \neq 1$ and is non zero, Eq. 5 can be integrated to give

$$(y_0 - cPA)^{1-n} - (y_0 - cPA_0)^{1-n} = (n-1)k_0 te^{-E/RT} \tag{6}$$

Dividing by $(cP)^{1-n}$:

$$\left[\frac{y_0}{cP} - A\right]^{1-n} - \left[\frac{y_0}{cP} - A_0\right]^{1-n} = \frac{(n-1)k_0 te^{-E/RT}}{(cP)^{1-n}} \tag{7}$$

The boundary conditions require that the peak area go from a minimum to a maximum, as cure time varies from zero to infinity. Thus, at the lower bound ($t = 0$) the peak area must be a minimum, and the difference between the two terms on the left-hand side of Eq. 7 must equal zero. Therefore, at zero cure time the minimum area is equal to A_0 (minimum $A = A_0$ at $t = 0$). At the upper bound ($t \to \infty$, E/RT finite), the peak area should be a maximum, and the

Table 1 - Values of Constants from Chemical Kinetic Model

A_O	= 9.7%
A_M	= 19.0%
E	= 19,900 cal/mole
n	= 2
B	= 6×10^7/hr

Table 2 - Calculated Area of Peak A from Model Equation

(Deviation Of Test Data In Parentheses)

	Time, hr				
	1	2	4	8	16
Temperature, F					
250	9.75 (-0.1)	9.80 (-2.3)	9.90 (-1.9)	10.09 (-1.2)	10.45 (-0.05)
287	9.87 (+0.2)	10.04 (-0.1)	10.36 (-0.4)	10.93 (-1.6)	11.87 (-0.9)
350	10.73 (-1.4)	11.56 (+0.1)	12.79 (-0.6)	14.34 (-0.05)	15.89 (+0.3)
400	12.60 (+0.1)	14.12 (-0.5)	15.70 (+1.5)	16.99 (+0.2)	17.87 (-0.3)

left-hand side of Eq. 7 should approach infinity. This can occur only if the maximum peak area is y_0/cP (maximum $A = y_0/cP$).

Let A_M denote the peak area for a maximum cure sample, and for convenience, let a new constant $B = (n - 1)\, k_0/cP^{1-n}$. Substituting the above terms into Eq. 7 gives the following:

$$(A_M - A)^{1-n} - (A_M - A_0)^{1-n} = Bte^{-E/RT} . \quad (8)$$

The form of Eq. 8 is compatible with the observed PGC phenol peak area. A computer solution of Eq. 8, utilizing curve fitting techniques, resulted in the curves shown in Fig. 6. The PGC data can be expected to include some variance due to sample, procedure, and instrument effects. A normal distribution of these variances was assumed; hence the values of A_0, A_m, n, B, and E were sought which minimized the sum of the squares of their absolute differences between model and test data. The best set of values obtained by the curve fitting is given in Table 1.

The calculated values of peak area and the deviations from the experimental values are given in Table 2.

The literature value for the activation energy for methylene bridge formation is 13.7 Kcal/g mole. (5) With cross-linking, there would be multiple bond formation, thereby increasing the activation energy. Also, hexa reacts with phenolic resin to form aromatic amines which again would influence the activation energy. Thus, a value of 19.9 Kcal/g mole for the activation energy is quite reasonable.

INDEX OF CURE - An index of cure can be defined which reduces the time/temperature curing conditions to a single parameter. It is defined as:

$$I_c = \frac{A - A_0}{A_M - A_0} \times 100 . \quad (9)$$

This equation is based on the assumption that samples with the same phenol peak area have a similar "state of cure." Calculated values of the index of cure are given in Table 3 for this oil-modified, phenolic resin system. For example, it appears that a sample cured for 4 hr at 350 F has a similar state of cure to one cured for 1 hr at 400 F. Preliminary comparisons between the values of cure index and FAST wear (total weight loss) and friction indicate a strong qualitative agreement for this resin system. This will be illustrated in a later section.

Table 3 - Index of Cure

	Time, hr				
	1	2	4	8	16
Temperature, F					
250	0.5	1	2	4	8
287	2.0	3.5	7	13	23.5
350	11	20	33	50	66.5
400	31	47.5	64.5	78.5	88

FUNCTIONAL RESPONSES TO CURE CONDITION CHANGES

CURE TIME AND TEMPERATURE EFFECTS - The FAST machine test procedure used was able to show significant changes in the friction and wear behavior due to the varying cure conditions studied.

Fig. 8 shows the sample weight loss during the FAST test plotted versus cure time, with cure temperature as parameter. The effect of cure temperature on total sample wear increases nonlinearly with temperature in the same manner as the PGC response described previously. The cure time effect on wear is also similar to the PGC response; that is, the effect is greatest for the low cure times and rapidly diminishes above the 4 hr cure time. The solid curves shown represent the best fit to the data of an equation of the same form as was used to generate the PGC peak areas from the mathematical model of the cure kinetics.

Fig. 9 shows four of the friction traces from the FAST machine and illustrates the type of friction differences found. There was generally a slight overall increase in friction level with increasing cure, especially at the higher test disc temperatures (> 500 F). A rational interpretation can be made of the friction variations during the beginning of the test. Variations which occur during the first three minutes of the test may be disregarded due to seating and surface conditioning effects. The variations during the remainder of the test can be attributed to the cure variations. Beyond 20 or 30 minutes, the cure effects diminish as the materials approach the same state of cure due to the heat generated at the friction interface.

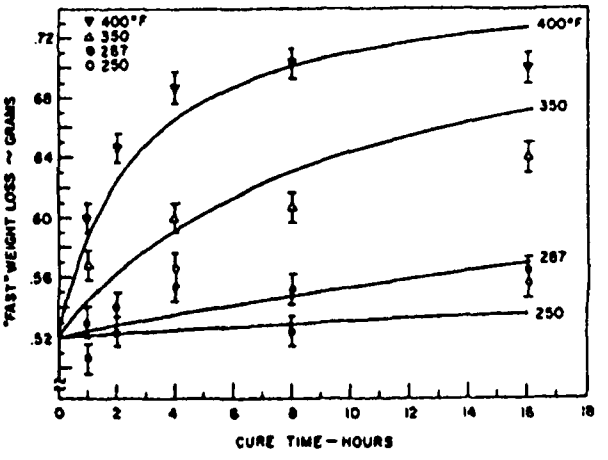

Fig. 8 - Variation in FAST wear with cure conditions

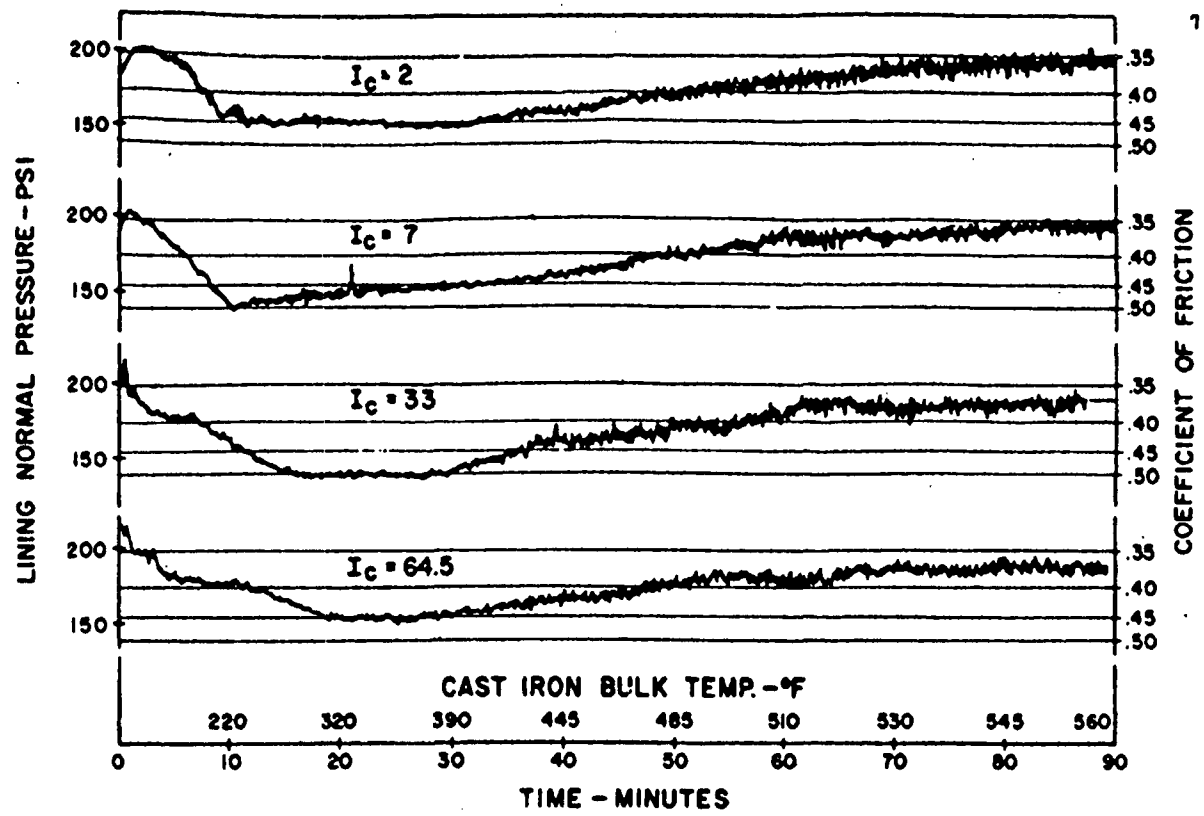

Fig. 9 - Variations in FAST friction with changing index of cure -- complete test traces

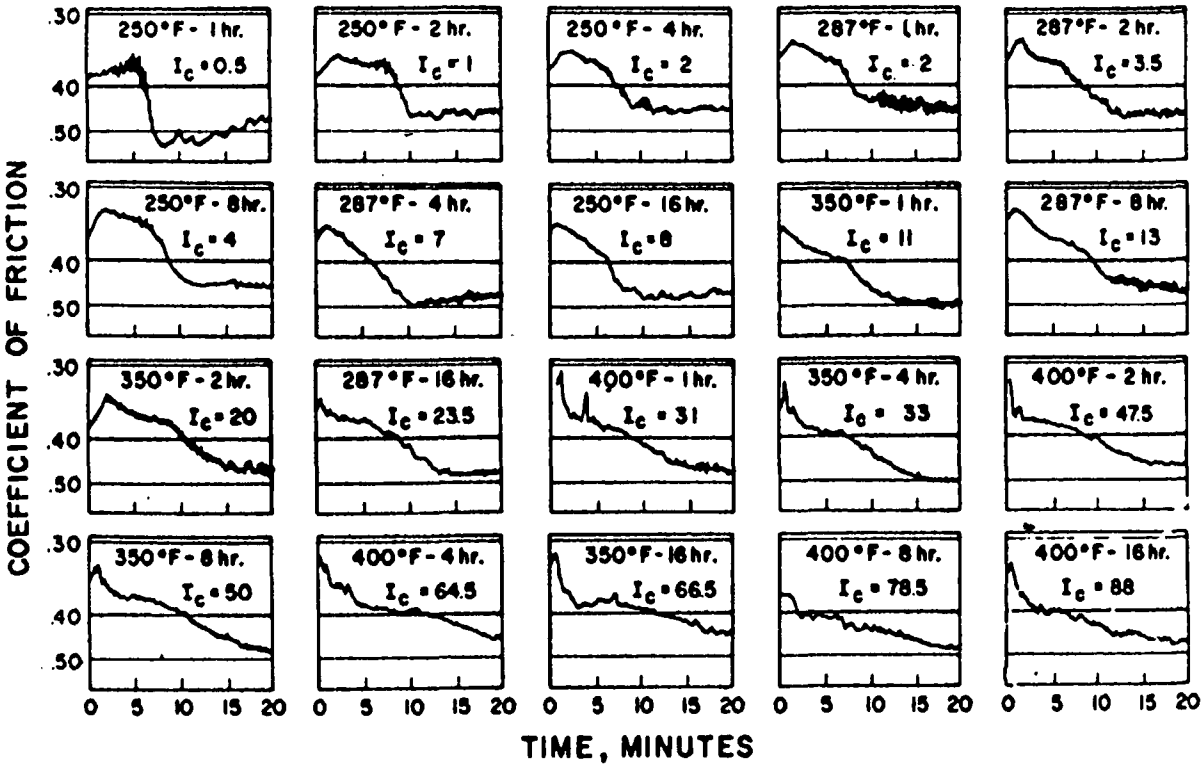

Fig. 10 - Variations in FAST friction with changing index of cure -- initial 20 minutes

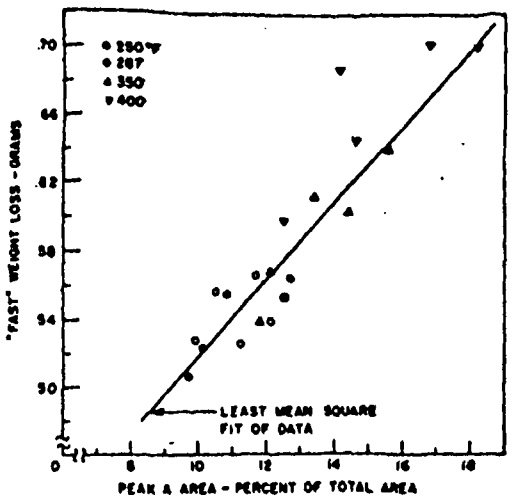

Fig. 11 - Correlation between area of Peak A and FAST weight loss

The first 20 minutes of the test results are shown in Fig. 10 for all the cure conditions studied. These curves are arranged in order of the sample's "index of cure," as defined in the preceding section. A systematic change in shape with increasing index of cure is readily apparent. The amount of change between cure conditions from the steplike shape of the 250 F cure sample friction traces to the sloping shape of the 400 F cure sample friction traces is qualitatively consistent with the values of the index of cure noted on each curve.

CURE AGENT CONCENTRATION EFFECTS - Friction and wear variations due to varying the cure agent concentration in the material were small compared to the effects of cure time and temperature.

In general, those samples cured at 250, 300, or 350 F had slightly decreased wear with excess hexa (20%) when compared with the low hexa samples (10%). At the 400 F cure, the increased hexa had a slightly detrimental effect, and the wear rate was greater than for the low hexa samples. The 15% hexa level wear results generally fell between the 10% and 20% results and were qualitatively consistent with the results of the first group of samples.

The friction differences between the low and high hexa samples were greatest for the low temperature cures where the high hexa (20%) samples had slightly lower friction than the low hexa samples. This effect occurred for about the first 30 minutes of the test, after which there were no effects clearly attributable to hexa level.

These friction and wear results are consistent with known vehicle performance; that is, the cure effects upon friction rapidly diminish with use, while the effects on wear affect the lining for a much longer time.

INTERRELATIONSHIP BETWEEN FAST AND PGC

As previously shown, both the FAST friction and wear data and the PGC peak A area show systematic changes with increasing degree of cure. To demonstrate the relationship between the chemical cure variations as detected by PGC and the functional variations in the form of FAST results, the area of peak A is shown in Fig. 11 plotted against FAST total sample weight loss. The solid line represents the linear fit to the data which provides a correlation coefficient of 0.93. The mean error from the linear fit is 3.23%, with the maximum deviation of 10% occurring for the 4 hr 400 F cure.

These results illustrate that chemical changes detectable by PGC are functionally significant, at least, in the system investigated in this study. For this resin system, variations in the curing conditions produced a corresponding variation in the FAST wear. That is, increasing the cure results in an increase of both the phenol peak area and wear. This provides important support for the use of these two methods for both quality assurance and laboratory testing.

SUMMARY AND CONCLUSIONS

An oil-modified, phenolic resin-asbestos system was used to study the chemical and functional responses to variations in cure conditions. Five cure times at each of four cure temperatures were investigated using pyrolytic gas chromatography (PGC) and the friction assessment screening test (FAST).

The PGC results show a systematic variation with changes in cure time and temperature.

The FAST friction and wear results show a systematic variation with cure time and temperature consistent with the PGC response.

For this resin system, a linear relationship exists between the area of the phenol peak, as determined by PGC, and the wear determined by the FAST procedure.

A chemical kinetic model is postulated which relates the concentration of phenol produced on pyrolysis to a function of cure time and temperature. The model accurately fits the actual phenol concentration as determined by PGC.

An index of cure is defined which reduces the curing conditions to a single parameter consistent with the functional test.

Variations in cure agent concentration influence the PGC and FAST responses, but in a more complex manner than the cure time and temperature variations studied.

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