

## Protection Against Intense Light. II. The Role of the Gaseous Decomposition Products

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### Synopsis

Screening studies have shown that of a series of halogenated vinyl polymers, poly(vinylidene fluoride) gives comparatively good thermal protection when exposed to the intense light energy of the carbon arc-image furnace. Results indicate that this protection is undoubtedly provided by polyenes,  $-(CH=CF)_n-$ , formed during pyrolysis. Decomposition products containing these structures are expelled by the gases formed into the region between the light source and the target where they intercept photons from about 200 to 500  $m\mu$  and dissipate the energy to the air as heat and/or reradiate it. Instrumental evidence for polyene formation is given. The concept of polyene formation clarifies the relative thermal protection offered by a series of vinyl polymers.

### INTRODUCTION

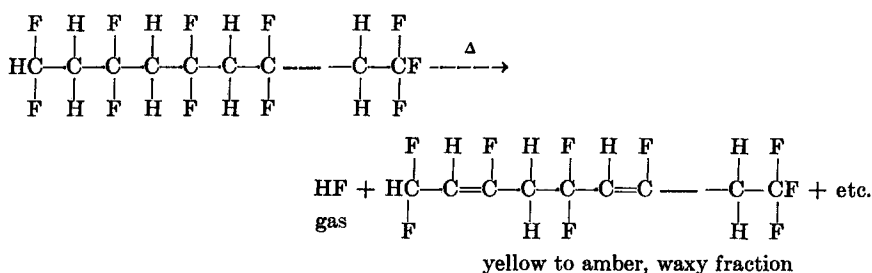
In a prior article<sup>1</sup> the relative thermal protection offered by a series of halogenated vinyl polymers was analyzed in terms of the usual modes of energy attenuation and dissipation. It was shown that none of these modes individually could account for the data. This article is concerned with the gaseous decomposition products and their role in thermal protection. In particular, it will be shown that certain polymers can automatically generate a significant measure of thermal protection on exposure to intense thermal radiation by the following mechanism: (a) the polymer decomposes, yielding a gas and compounds containing chromophoric groups; (b) the compounds containing chromophoric groups vaporize and expand or are propelled by the gas into the region between the polymer target and the source of radiant energy; (c) the compounds containing chromophoric groups intercept photons and reradiate or dissipate the energy to the air as heat, thereby protecting the target.

In the search for means of protection from the intense thermal energy of a thermonuclear explosion, it was established by Barnes and Yelland<sup>2</sup> that, of the polymers listed in Table I, poly(vinylidene fluoride) (PVF<sub>2</sub>) provided the best protection. This was determined by preparing ten discs of each polymer. Each disc was 0.060 in. thick and 2 in. in diameter and contained 5% of a colored additive, powdered Cr<sub>2</sub>O<sub>3</sub>, to make it opaque. These discs were then exposed to a single elliptical, carbon arc-image furnace<sup>1</sup> at an irradiance level of 23 cal/cm<sup>2</sup> for 1 sec. The temperature

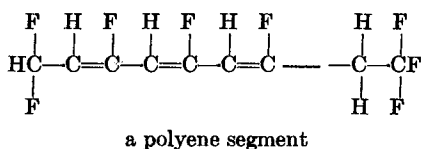
rise,  $\Delta T$  (in  $^{\circ}\text{C}$ ), above ambient of a thermocouple placed on the rear surface of the disc was measured, the ten values were averaged, and the frequency of ignition of the decomposition products computed.<sup>2</sup> This information is listed in Table I together with the polymer abbreviations to be used.

### THERMAL BEHAVIOR OF POLY(VINYLDENE FLUORIDE)

The thermal behavior of  $\text{PVF}_2$  will be used to illustrate the mechanism described above. When pyrolyzed,  $\text{PVF}_2$  yields copious quantities of gases including HF, and a yellow to amber wax distillate in addition to char. Obviously, since the wax is colored, it absorbs light. A representative reaction is



Now, since the allylic position is relatively weak, more HF should split off under the intense heat, so that the above reaction will proceed readily and some of the molecules with two double bonds will lose HF to produce



which is a molecule with three conjugated double bonds, i.e., a polyene segment. This and similar processes can continue anywhere in the degraded polymer chains (amber wax), producing longer conjugation which will in turn intercept light of longer wavelengths. As the conjugated sequences get longer, however, their relative amounts should decrease simply because the probability of obtaining six conjugated double bonds is much less than the probability of obtaining only two conjugated double bonds.

Those molecules in the amber, waxy fraction which contain conjugated unsaturation (polyenes), together with the vast majority of molecules which undoubtedly do not, are propelled by the gases and/or expand into the region between the polymer disc and the carbon arc-image furnace, where they vaporize if they have not already done so. Here, the molecules with conjugated unsaturation intercept those photons which lie within their absorption spectrum, go to a higher energy level, dissipate the energy to the air as heat, and/or reradiate it via successive vibrational and rotational states while returning to the ground state. Then they pick up a second

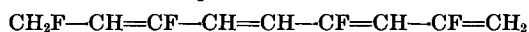
TABLE I  
Polymers and Their Performance in the Carbon Arc-Image Furnace

Polymer	Repeating unit	Av. $\Delta T$ , °C	Freq. of ign., %
Poly(vinyl chloride) (PVC)	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{Cl} \end{array}$	22.3	100
Poly(chlorotrifluoroethylene) (Kel-F)	$\begin{array}{c} \text{F} \quad \text{F} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{F} \quad \text{Cl} \end{array}$	13.0	0
Poly(vinyl fluoride) (PVF)	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{F} \end{array}$	16.8	100
Polyethylene (PE)	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{H} \end{array}$	19.2	100
Poly(trifluoroethylene) (PVF <sub>3</sub> )	$\begin{array}{c} \text{F} \quad \text{F} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{F} \end{array}$	11.3	0
Poly(vinylidene fluoride) (PVF <sub>2</sub> )	$\begin{array}{c} \text{H} \quad \text{F} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{F} \end{array}$	10.8	50
Teflon (PVF <sub>4</sub> )	$\begin{array}{c} \text{F} \quad \text{F} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{F} \quad \text{F} \end{array}$	36.3	0

light photon and repeat the cycle indefinitely until they degrade, ignite, or are blown away. The half-life of the cycle will "generally vary down to  $10^{-7}$  to  $10^{-9}$  seconds."<sup>3</sup> Obviously, for this mechanism to operate efficiently, the material containing the chromophoric groups should be dispersed as individual molecules and should be stable in air at elevated temperatures. Of the chromophoric groups listed by Noller<sup>4</sup>:  $\text{NO}_2$ ,  $\text{C}=\text{O}$ ,  $\text{N}=\text{N}$ ,  $\text{C}=\text{C}$ ,  $\text{C}=\text{N}$ ,  $\text{C}=\text{S}$ , and  $\text{N}=\text{O}$ , the only chromophoric group which can be present in the amber, waxy fraction is  $\text{C}=\text{C}$ , because there is no nitrogen, oxygen, or sulfur in the polymer.

### EXPERIMENTAL RESULTS

There is considerable evidence of the presence of unsaturation in the pyrolysis products of PVF<sub>2</sub>. Mass spectrometry of the gaseous pyrolysis products of PVF<sub>2</sub> indicated the presence of



Note the presence of four conjugated double bonds. Also, practically all of the gaseous decomposition products contained unsaturation.<sup>5</sup>

Examination of the yellow, waxy fraction showed:

1. Assuming the formation of one double bond for every ten carbon atoms, the elemental analyses calculated and found are as follows:

ANAL. Calcd: C, 40%; F, 57%; H, 3%. Found: C, 39.5%, 40.7%; F, 57.5%, 56.1%; H, 3.02%, 3.17%.

Since there is about one multiple bond for ten carbon atoms, there is a good chance for a small amount of conjugation.

2. IR absorption in the  $1590$  to  $1680\text{ cm}^{-1}$  region is strong. Absorption in this region is characteristic of conjugated unsaturation.<sup>6</sup>

3. The curves in Figure 1 show the carbon arc emission spectrum<sup>16</sup> and the per cent transmission of a 5% solution of the amber, waxy fraction in spectroscopic-grade *p*-dioxane using a 1-cm path length cell. UV transmission is less than 1% from 200 to 400  $m\mu$  and then rises rather rapidly with increasing wavelength. Polyenes (hydrocarbon) show intense absorption up to 370  $m\mu$  where the absorption decreases rapidly.<sup>7</sup> Thus, the behavior of the amber, waxy fraction in the UV conforms to that expected from polyenes.

4. As stated above, as the number of conjugated double bonds in the polyene decreases, the relative amount of that polyene should increase, i.e., there should be more polyenes containing three double bonds than there

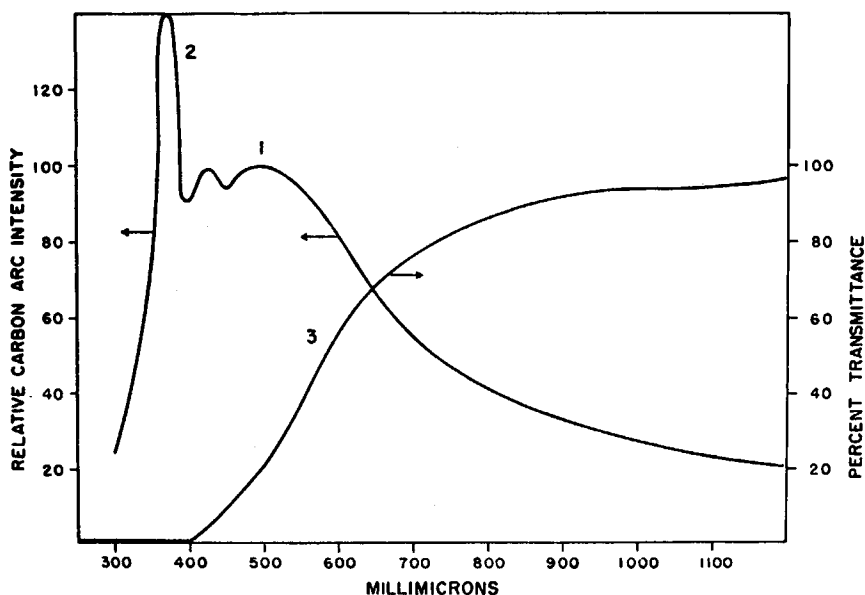


Fig. 1. Relative carbon arc intensity and per cent transmittance vs. wavelength, in millimicrons: (1, 2) carbon arc emission spectrum; (2) carbonyl bands; (3) per cent transmission of a 5% solution of the condensable fraction from the arc pyrolysis of poly(vinylidene fluoride) in spectroscopic-grade 1,4-dioxane.

are polyenes containing six double bonds. Hence, the UV absorbance curve should peak where butadiene peaks, at  $217 \text{ m}\mu$ ,<sup>3</sup> and it does.

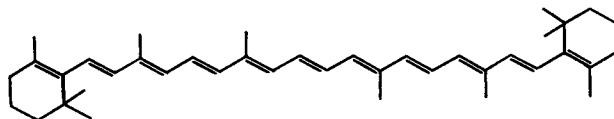
5. Since the wax is yellow, it must absorb blue light, and, consequently, chromophores must be present. As pointed out above, these very probably consist of linear, conjugated unsaturation.

6. On standing for a period of time, the wax hardens, just as paint "dries," by oxidation at double bonds.

For a given concentration of the polyene groups, there is some thickness of the waxy fraction at which 99.9% of the thermal energy that lies within the absorption spectra of the polyene groups is intercepted. The amount of light transmitted will not be changed very much by increasing the thickness, so that absorption in the same region is 99.999%. The point is that above some thickness the light transmitted will be substantially independent of thickness, i.e., the light transmitted will not be substantially diminished.

The approximate amount of light that should be transmitted by a "thick" layer of the amber, waxy fraction can be estimated from the curves of Figure 1, assuming that a 5% solution corresponds to a "thick" layer. The product of the per cent transmission and emission at each abscissa can be plotted. The area under the resulting curve is a measure of the energy transmitted and amounts to about 50%. In any case, if one is to accept the hypothesis that the polyenes in the amber, waxy fraction are responsible for most of the thermal protection afforded, a "thick" layer of the fraction should intercept a reasonable portion of the incident light based on the known behavior of polyenes (see paragraph 3 above) and the above estimate. When a thickness (approximately 0.04 in.) which would correspond to a UV cell concentration greater than 5% was tested, 55% of the light from the arc was absorbed. Thus, the yellow, waxy fraction absorbs a significant portion of the thermal energy, and conjugated unsaturation is, therefore, a major factor in the behavior of PVF<sub>2</sub> toward intense light energy.

As a check of this concept, a saturated solution of a diphenyl polyene,  $\beta$ -carotene,



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in a polyacrylate dissolved in a solvent was prepared using an excess of the  $\beta$ -carotene. The solvent was evaporated leaving an amber disc about  $1/16$  in. thick and 2 in. in diameter, which contained  $0.12 \text{ mg polyene/cm}^2$ .

$\beta$ -Carotene absorbs strongly from about  $390$  to  $500 \text{ m}\mu$ ,<sup>3</sup> and weakly at bordering wavelengths. The molar absorptivity ( $\epsilon_{\text{max}}$ ) at the wavelength of maximum absorption ( $\lambda_{\text{max}}$ ) is  $150,000$  and  $460 \text{ m}\mu$ , respectively. From

Figure 1, one would estimate that no more than 50% of the light of the carbon arc should be absorbed. On testing, using a clear control, about 40% of the light of the carbon arc was absorbed. Blisters were raised, but no char was formed. There is then no question that a polyene, protected from, or stable to, oxidation and dispersed as molecules, will absorb a significant fraction of the light energy of the arc.

### DISCUSSION

Polyenes can be quite efficient in intercepting photons inasmuch as the weight of polyenes required to absorb a significant fraction of the incident light energy is quite small. As an example, consider the cyanogen bands of the carbon arc-image furnace (and peculiar thereto) at about 360, 390, and 420  $m\mu$ . The combined bands at 360 and 390  $m\mu$  are 40–50% more intense than any other span of equal width in the carbon arc emission spectrum. The molecule,  $\text{H}-(\text{CH}=\text{CH})_6-\text{H}$ , a polyene, has a  $\lambda_{\text{max}}$  at 364  $m\mu$ ; its absorption spectrum overlaps the two lower cyanogen bands. It has a molar absorptivity ( $\epsilon$ ) of 138,000.<sup>3</sup> Assuming that  $-(\text{CH}=\text{CF})_6-$ , a structure which could occur in the amber, waxy fraction, has the same properties, the amount of material required to reduce the light intensity to 1/10,000 of its initial value (an absorbance or optical density of 4) can be computed using the Lambert-Beer law,

$$\log_{10} (I_0/I) = \epsilon cb = \text{absorbance} = \text{optical density}$$

where  $I_0$  is the initial light intensity,  $I$  is the intensity of transmitted light,  $\epsilon$  is the molar absorptivity,  $c$  is the concentration in moles per liter, and  $b$  ( $= 1$  cm) is the path length through the sample in centimeters:

$$\log_{10} (10,000/1) = 138,000 \times c \times 1$$

$$c = 2.9 \times 10^{-5} \text{ moles/l.}$$

$$c = 2.9 \times 10^{-8} \text{ moles/cc.}$$

Since the molecular weight of  $\text{H}-(\text{CH}=\text{CF})_6-\text{F}$  is 284 g, the weight of this material required to block 99.99% of the light in the 364- $m\mu$  region and thereby to protect 1.0  $\text{cm}^2$  of the polymer disc from light in that region is

$$\begin{aligned} 2.9 \times 10^{-8} \times 284 &= 8.22 \times 10^{-6} \text{ g} \\ &= 8.22 \text{ micrograms.} \end{aligned}$$

Since the weight of the amber, waxy fraction produced during a 1-sec exposure to the arc is about 26 mg,<sup>8</sup> it is entirely possible for such a small quantity of polyene linkages,  $-(\text{CH}=\text{CF})_6-$ , to arise. It is even more probable that shorter ( $n = 2, 3, 4,$  and  $5$ ) polyene segments will also be produced in even greater amounts.

Since an optical density of 4 was assumed, the amount of light energy in the combined cyanogen bands at 360 and 390  $m\mu$  penetrating the vapor-

ized pyrolysis products and striking the PVF<sub>2</sub> disc can now be estimated. From Figure 1, it is apparent that the energy of the combined cyanogen bands is less than 30% of the energy emitted by the arc, or, for 1 sec, less than 6.9 cal. The amount of energy penetrating the 2,4,6,8,10,12,12-heptafluorododeca-1,3,5,7,9,11-hexene, H—(CH=CF)<sub>6</sub>—F (or the analogous segments in the amber waxy fractions), is, therefore, less than 0.00069 cal. (On a bright day, the intensity of sunlight is about 0.02 cal/cm<sup>2</sup>-sec.)

Consequently, once the waxy fraction appears in the region between the PVF<sub>2</sub> disc and the light source, practically all of the energy below about 400 mμ and about  $\frac{1}{3}$  of the light energy above 400 mμ should be intercepted and dissipated to the air as heat. In general, materials usable in the above manner which have a high molar absorptivity, i.e., "loosely" held electrons, such as polyenes, cumulenes, ferrocene, and its derivatives, tetraphenyltin, tetraphenyllead, tungsten and molybdenum carbonyls, dyes, pigments, etc., should provide good thermal protection.

The following have now been established for PVF<sub>2</sub>: (a) the manner in which polyenes can be generated, (b) their presence in the waxy fraction of the decomposition products, (c) the possibility of the interception of a significant portion of the incident energy by the waxy fraction, and (d) the low weight of the polyenes required to intercept this energy compared to the weight of the waxy fraction. Hence, it is possible that dyes can be involved in thermal protection. For brevity, dyes will be defined as compounds containing chromophoric groups, and both will be defined to be any substance, material, or compound which intercepts photons and possibly fluoresces. The final and most important question that must be answered is: Is there any correlation between dye formation and  $\Delta T$  values?

It will now be shown that energy attenuation by chromophoric groups (primarily, if not entirely, polyenes) operating according to the mechanism postulated (where applicable) is the controlling factor determining the relative  $\Delta T$  values presented in Table I. (All the polymer discs contain powdered Cr<sub>2</sub>O<sub>3</sub> (5% level), which is green to make the transparent polymers opaque.)

PVF<sub>2</sub> produces the most HF and, therefore, probably the greatest quantity of molecules containing conjugated unsaturation of all the hydrofluoropolymers, including PE and Teflon, of course. If such molecules are a major factor in energy dissipation, then PVF<sub>2</sub> should have the lowest  $\Delta T$  value, which it does. The fact that its  $\Delta T$  value is the lowest despite the fact that the frequency of ignition was 50% strongly indicates that the conjugated sequences survived the flames.

It is apparent that HF can split off from PVF<sub>3</sub> in the same manner as from PVF<sub>2</sub>. Consequently, PVF<sub>3</sub> should also have a low  $\Delta T$ , and it does. After removal of HF, the conjugated sequences consist solely of carbon and fluorine. Consequently, the frequency of ignition should be low, which it is.

When HF splits off from PVF, unsaturated hydrocarbon segments are formed which should ignite readily, destroying the conjugation, and gen-

erate copious smoke. Consequently, the  $\Delta T$  for PVF should be above that of  $PVF_2$  and  $PVF_3$ , the frequency of ignition should be high, and much smoke should be produced, all of which occur.

When PVF,  $PVF_2$ , and  $PVF_3$  were each pyrolyzed under vacuum, all three yielded "a nonvolatile, light-brown wax-like deposit soluble in acetone."<sup>9</sup> Consequently, the pyrolyzate of PVF and  $PVF_3$  must also absorb blue light and hence have molecules with chromophoric groups, most of which are very probably polyenes.

Thermal protective creams containing halogenated chemicals compounded at the U.S. Army Natick Laboratories have shown excellent thermal protection when exposed to the highest intensity of the carbon arc-image furnace for periods up to 6 sec.<sup>10</sup> Copious quantities of decomposition products were generated which expanded toward the light source. One of the ingredients of these creams is poly(chlorotrifluoroethylene) (Kel-F).<sup>11</sup> On pyrolysis, Kel-F yields the same yellow-amber, waxy fraction<sup>12</sup> as do  $PVF_2$ ,  $PVF_3$ , and PVF,<sup>9</sup> which indicates the presence of chromophoric groups, and a gas, monomeric trifluorochloroethylene.<sup>12</sup> Since the fluorine decolorizes the waxy fraction,<sup>12</sup> the chromophoric groups probably contain conjugated unsaturates. With a zero frequency of ignition, the  $\Delta T$  value should be below that of PVF and PE, which is the case.

Since PE, on pyrolysis, should not yield significant amounts of conjugated unsaturation compared to  $PVF_2$  and  $PVF_3$ , its  $\Delta T$  value should be higher, and it is. In this case the usual energy sinks such as endothermic decomposition, loss of high temperature material, etc., are the controlling factors.

The case of poly(vinyl chloride) (PVC) is interesting in that it shows an average  $\Delta T$  of 22.3°C, which is rather high, and ignites 100% of the time. Since PVC loses HCl so readily,<sup>13</sup> one would expect to obtain a very high degree of unsaturation and a very low  $\Delta T$  value. Practically all of the HCl comes off at temperatures as low as 220°C.<sup>14</sup> Pyrolysis of PVC yields a volatile fraction consisting of 96.3% HCl, 2.7% benzene, 0.1% toluene, and 0.9% other hydrocarbons.<sup>14</sup> There is a fundamental difference in the pyrolysis behavior of this polymer, however, in that no fraction condensed at room temperature,<sup>14</sup> indicating that relatively few carbon-carbon bonds were broken. What is undoubtedly happening is that the benzene and toluene produced ignite during pyrolysis in the carbon arc-image furnace, producing smoke as would be expected, but the unsaturated, highly conjugated material (which probably crosslinks) remains attached to the surface of the polymer disc where it absorbs the light from the arc very efficiently, producing a high  $\Delta T$  value. Here again the conjugated sequences are hydrocarbons, so that even if any of them are ejected in front of the disc, they will provide little protection because they will be consumed by the flames as in the case of PVF. Energy dissipation by the PVC system is probably by endothermic decomposition, resulting in the expulsion of HCl and other gases, which also carry a sizable amount of energy as kinetic energy; scattering of light by smoke should help somewhat.





Again the PVF<sub>2</sub>- and PVF<sub>3</sub>-type polyenes should be obtained and good thermal protection result. Although it is not clear what fragments ignited, the fact that a low  $\Delta T$  value of 6.5°C was obtained indicates that the polyenes formed survived the flame as in the case of PVF<sub>2</sub>. If the polyenes had decomposed immediately, one would expect to get approximately the  $\Delta T$  value of PVF, 16.8°C.

It is not implied that the postulated mechanism is absolutely necessary for a substance to provide good thermal protection. In the prior paper<sup>1</sup> it was pointed out that the nitroso rubber system gave good thermal protection. Thermal protection by char formation was ruled out since there was no char formed. Because the primary pyrolysis products are CF<sub>2</sub>=O and CF<sub>2</sub>=N—CF<sub>3</sub>, both of which have low molar absorptivities, thermal protection by the formation of compounds containing chromophoric groups also can be tentatively ruled out. (Since small amounts of other pyrolysis products may be produced which have high molar absorptivities, dye formation is not eliminated. There simply is no evidence for or against it. Nitroso compounds can have high molar absorptivities.<sup>1b</sup>)

## CONCLUSION

Since the waxy fraction intercepted a significant percentage of the light from the carbon arc-image furnace, and the mechanism postulated in the introduction does clarify the relative  $\Delta T$  values in Table I, there is little if any doubt that energy attenuation by this mechanism is the dominant factor in these experiments. This leads one to surmise that compounds containing chromophoric groups (dyes) can be formed which can survive elevated temperatures long enough to provide substantial thermal protection against the intense light energy of a thermonuclear explosion.

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