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Study of etching and annealing characteristics of ^{238}U ion tracks in Trifol-TN polycarbonate

R K Jain†, G S Randhawa‡, S K Bose§ and H S Virk†

† Department of Physics, Guru Nanak Dev University, Amritsar 143 005, India
‡ Department of Physics, Khalsa College, Amritsar 143 003, India
§ Department of Physics, BHU, Varanasi 221 005, India

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Abstract. The etching and annealing characteristics of heavy ion irradiated Trifol-TN polycarbonate plastic were studied. The values of various etching parameters, namely bulk etch rate (V_G), track etch rate (V_T), critical angle (θ_c), sensitivity (S), etching efficiency (η) and activation energies for bulk (E_b) and track etching (E_t) are reported. The isochronal annealing was performed on ^{238}U (17.17 and 16.34 MeV u^{-1}) ion-irradiated Trifol-TN plastic. The annealing kinetics of heavy ion damaged Trifol-TN is described by using various empirical formulations. Finally, the experimental range of ^{238}U ions in Trifol-TN has been compared with the calculated values from different formulations.

1. Introduction

The production of tracks by energetic heavy ions in various nuclear track recording materials and their subsequent revelation by chemical etching is widely used in science and technology (Fleischer *et al* 1975). A number of new latent track recording materials, namely glasses, minerals, plastics etc, have been reported in the literature (e.g. Cartwright *et al* 1978, Price and Tarle 1985, Price *et al* 1987a, Fujii *et al* 1988, Wang *et al* 1988). The class of plastic track recorder, CR-39, discovered by Cartwright *et al* (1978) has been used in a wide range of applications because of its high detection sensitivity and charge resolution. In the last few years thin sheets of plastic track recording materials have been used to produce single- and multipore filters having remarkable applications in environmental, biomedical sciences and microtechnology (Fischer and Spohr 1983, Spohr 1990). Makrofol-N ($C_{16}H_{14}O_3$ density $\sim$1.23 g cm^{-3}) and Trifol-TN ($C_3H_4O_2$, density = 1.153 g cm^{-3}) manufactured by Bayer Co., Germany, have been found to be very useful in such applications due to their non-brittle nature unlike CR-39 and other plastic materials such as SR-86, Tastrack etc.

In the present paper the etching and annealing kinetics of ^{238}U (17.17 and 16.34 MeV u^{-1}) ion tracks in a polycarbonate plastic (Trifol-TN) were investigated. The values of various etching parameters, namely bulk etch rate (V_G), track etch rate (V_T), critical angle (θ_c), sensitivity (S) of the plastic for registration of ^{238}U ions, etching efficiency (η) and activation energies for bulk (E_b) and track etching (E_t) are reported. For study of annealing characteristics, the isochronal experiments were performed on Trifol-TN plastic irradiated with ^{238}U (17.17 and 16.34 MeV u^{-1}) ions from the UNILAC accelerator at GSI. The annealing kinetics of heavy ion damaged Trifol-TN is described by using modified version of the Modgil and Virk (1985) empirical formulation. Finally, the experimental range of ^{238}U ions in Trifol-TN has been compared with the calculated values obtained from different formulations.

2. Annealing mechanism

Knowledge of the annealing mechanism of nuclear tracks in thin sheets of polycarbonate and in crystalline minerals has become of increasing interest due to the wide applications of such tracks in fission track geochronology (Storzer 1970, Haack and Potts 1972, Sandhu and Westgate 1995). Most of the previous studies on thermal recovery of the damage have been restricted to the fission fragment tracks in minerals, glasses and plastics (Burchart *et al* 1979, Gold *et al* 1981, Mark *et al* 1981, Ritter and Mark 1983, Khan *et al* 1984, Green *et al* 1985). These studies do not reflect the exact picture of the etching and annealing mechanism because of the lower range, unidentified mass and energy and higher statistical errors inherent in fission fragment tracks, especially in case of plastics. So, for the present studies the behaviour of ion tracks in the Trifol-TN plastic produced using a well defined beam of ^{238}U (17.17 and 16.34 MeV u^{-1}) ions is investigated.

Modgil and Virk (1985) postulated a three-step annealing model which explains the annealing behaviour of radiation damage in bulk materials. The authors favoured the concept of a single activation energy of track annealing

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Table 1. Values of etching parameters, V_G, V_T, S, θ_c and η, of ^{238}U (17.17 and 16.34 MeV u^{-1}) ion tracks for unannealed Trifol-TN (etchant 6.0 N NaOH).

Energy (MeV u^{-1})	Etchant temp. (°C)	V_G (μm h^{-1})	V_T (μm h^{-1})	S (V_T/V_G)	η (%) ($1 - V_G/V_T$)	θ_c sin^{-1}(V_G/V_T)
17.17	40	0.49	12.4	24.90	95.98	2.30
	50	1.38	35.4	25.65	96.10	2.23
	60	3.02	76.2	25.25	96.01	2.27
	70	6.99	176.0	25.16	96.02	2.28
16.34	40	0.49	12.0	24.09	95.85	2.38
	50	1.38	36.6	26.52	96.23	2.16
	60	3.02	80.5	26.67	96.25	2.15
	70	6.99	186.0	26.58	96.24	2.15

and proposed an empirical formula

$$V_a = At_a^{-n} \exp(-E_a/kT_a) \quad (1)$$

where V_a is the annealing rate, dl/dt, i.e. the rate of change of track length, L, with relation to annealing time, A is the proportionality constant, k the Boltzmann constant, t_a and T_a are the annealing time and temperature respectively and E_a is the activation energy for the annealing of latent tracks.

In a paper on phosphate glasses Price *et al* (1987b) found that their annealing data could fit into the equation of Modgil and Virk provided the thermal annealing rate is replaced by the fractional thermal fading rate

$$\frac{(S-1)_i - (S-1)_f}{(S-1)_i} = At_a^{1-n} \exp(-E_a/kT_a) \quad (2)$$

where $S = V_T/V_G$ and subscripts i and f refer to the initial and final values. The authors have further proposed that by using this modified version of equation (1), the values of parameters A, n and E_a are reduced to certain constants for a given detector, irrespective of ion beam used. We took the challenge of testing this formulation on our recent data on annealing of ^{238}U ion tracks in the polycarbonate plastic Trifol-TN.

An attempt has been made by Bhatia and Virk (1989) to introduce a new parameter, instantaneous track etch velocity, in the left-hand side of equation (1) to improve upon the previous formulation as follows:

$$\frac{d(V_T/V_G)}{dt_a} = At_a^{-n} \exp(-E_a/kT_a) \quad (3)$$

where V_T/V_G is the track etch to bulk etch rate ratio for a particular annealing time and temperature and this formulation gives a best fit for annealing of heavy ion tracks in Lexan polycarbonate. Green *et al* (1985) have also formulated the concept of a single activation energy based on the results of annealing experiments on apatite. There are only a few reports on annealing in plastic track recording materials. It is true that the complex nature of plastics makes it difficult to present a satisfactory explanation of the annealing mechanism.

In this investigation we present comparisons of various etching parameters, namely bulk etch rate, V_G, track etch rate, V_T, sensitivity, S, critical angle of etching, θ_c, etching efficiency, η, before and after annealing. The activation energies for bulk etching, track etching and annealing have also been determined.

3. Experimental details

Different sets of Trifol-TN plastic track detectors were prepared for irradiation. These sets were exposed to ^{238}U (17.17 and 16.34 MeV u^{-1}) ion beams from the UNILAC accelerator at GSI, Darmstadt, Germany. The incidence angle of the beams with respect to the detector surface was 45°. Samples were annealed in a temperature-controlled oven with an accuracy of ±2 °C in the temperature range from 50 to 150 °C for a fixed interval of 30 min. The corresponding track lengths of both the unannealed and annealed samples were recorded after etching the different sets of samples in 6.0 N NaOH at different temperatures (40, 50, 60 and 70 °C).

4. Measurement of track etching and annealing parameters

For measuring the track etch rate V_T before and after annealing, the exposed samples (unannealed) were etched at various temperatures, namely 40, 50, 60 and 70 °C and the annealed ones at only 60 °C in 6.0 N NaOH by using a constant-temperature shaker water bath. After each etching interval, the samples were scanned under an optical microscope to record the projected etched track length at a magnification of 600×. The etching and microscopic observations were repeated until the maximum track lengths become invariant with further etching. The slope of the linear portion of the graphs (figures 1 and 2) give the track etch rates of different annealed and unannealed samples for ^{238}U ions 17.17 and 16.34 MeV u^{-1} respectively. The bulk etch rates were calculated by the relation (Durrani and Bull 1987)

$$V_G = \frac{\Delta x}{2\Delta t} \quad (4)$$

where Δx is the thickness of plastic dissolved in etching time Δt.

The track registration sensitivity is determined by using the relation V_T/V_G for ^{238}U (17.17 and 16.34 MeV u^{-1}) ion tracks in Trifol-TN and the etching efficiency, η, is determined by the relation

$$\eta = 1 - \sin\theta_c = 1 - V_G/V_T \quad (5)$$

where θ_c is the critical angle of incidence for track etching.

Table 2. Activation energy for bulk and track etching for ^{238}U ion irradiated Trifol-TN.

Energy (MeV u^{-1})	E_G (eV)	E_T (eV)
17.17	0.80	0.76
16.34	0.80	0.77

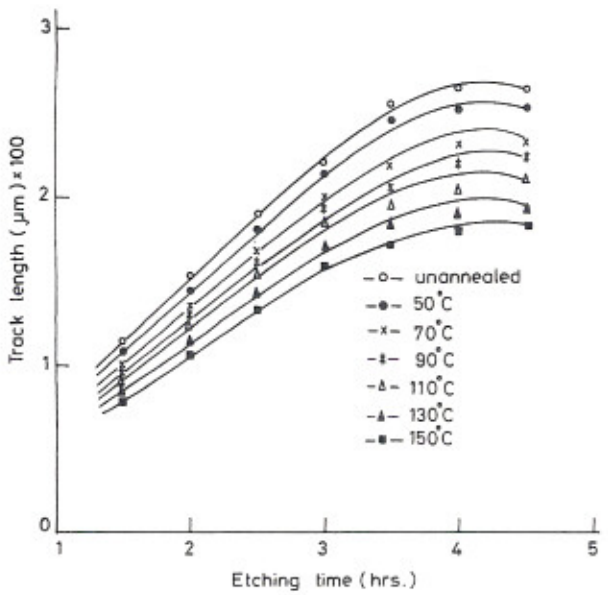

Figure 1. Variation of track length with etching time (etched in 6.0 N NaOH) for annealed and annealed Trifol-TN irradiated with ^{238}U (17.17 MeV u^{-1}) ions.

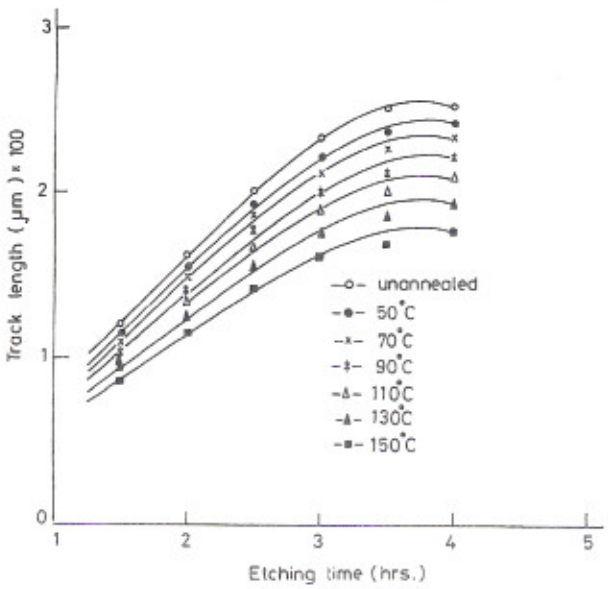

Figure 2. Variation of track length with etching time (etched in 6.0 N NaOH) for annealed and unannealed Trifol-TN irradiated with ^{238}U (16.34 MeV u^{-1}) ions.

The activation energy for bulk etching is calculated using the following relation (Enge *et al* 1975)

$$V_G = A \exp(-E_G/kT) \tag{6}$$

where V_G is the bulk etch rate for the unannealed sample,

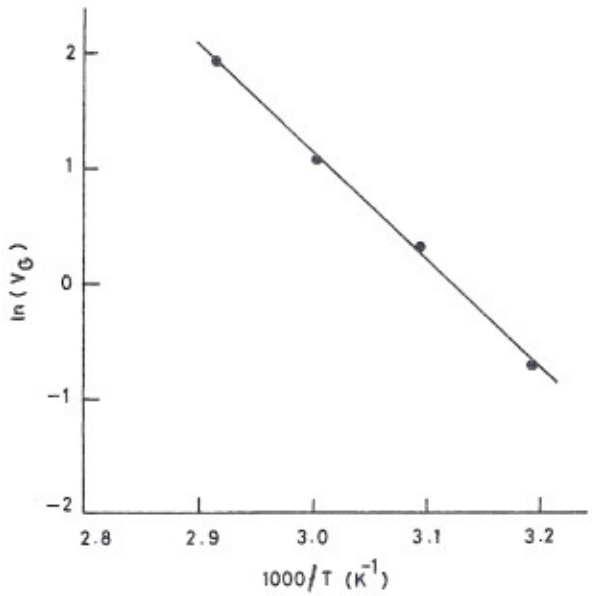

Figure 3. Plot of ln V_G versus 1000/T (K^{-1}) for unannealed Trifol-TN (etched in 6.0 N NaOH) for ^{238}U (17.17 MeV u^{-1}) ions.

E_G is the activation energy for the bulk etch rate, T is the etch temperature, k the Boltzmann constant and A is a proportionality constant. E_G is determined from the slope of the graph (figure 3).

The activation energy for track etching is calculated using following relation (Enge *et al* 1975)

$$V_T = B \exp(-E_T/kT) \tag{7}$$

where V_T is the track etch rate for the unannealed sample, E_T is activation energy for track etching and B, k and T have the usual meanings. E_T is determined from the slope of the graph (figure 4) for ^{238}U ions of energies 17.17 and 16.34 MeV u^{-1}.

For the determination of activation energy for the annealing of tracks of ^{238}U ion in Trifol-TN, equations (2) and (3) have been used. The activation energy of annealing, E_a, has been determined from the slopes of the graphs (figures 5 and 6) for ^{238}U ion of energy 17.17 MeV u^{-1} by using equations (2) and (3) respectively. The values of various etching parameters for unannealed samples, i.e. V_G, V_T, S, θ_c and η are given in table 1. The values of activation energy for bulk etching and track etching are presented in table 2. The various etching parameters for annealed samples are given in table 3.

Table 1 shows the etching parameters for ^{238}U ions of energies 17.17 and 16.34 MeV u^{-1} for unannealed samples. From this table it is concluded that V_G, the bulk etch rate, is the same for both the energies but increases with increasing temperature. The value of V_T also increases with increase of etchant temperature. The value depends upon the incident particle energy. The values of the track registration sensitivity, S, at different temperatures have been determined and found to be almost the same for a given ion energy. Hence, it can be concluded that for Trifol-TN the ratio V_T/V_G is generally independent of the etchant temperature. Table 2 gives activation energies for bulk and track

Table 3. Values of etching parameters, V_G, V_T, S, θ_c, and η, of ^{238}U (17.17 and 16.34 MeV u^{-1}) ion tracks for annealed Trifol-TN (etchant 6.0 N NaOH at 60 °C).

Energy (MeV u^{-1})	Annealing temp. (°C)	V_G (μm h^{-1})	V_T (μm h^{-1})	S (V_T/V_G)	η (%) ($1 - V_G/V_T$)	θ_c sin^{-1}(V_G/V_T)
17.17	50	2.95	72.0	24.40	95.90	2.37
	70	2.90	67.2	23.17	95.68	2.47
	90	2.87	65.1	22.68	95.59	2.52
	110	2.82	62.0	21.98	95.45	2.60
	130	2.75	56.9	20.69	95.16	2.77
	150	2.66	53.0	19.42	94.98	2.87
16.34	50	2.95	77.3	26.20	96.18	2.18
	70	2.90	75.2	25.93	96.14	2.21
	90	2.87	71.5	24.91	95.98	2.30
	110	2.82	67.3	23.86	95.81	2.40
	130	2.75	62.2	22.62	95.58	2.53
	150	2.66	57.3	21.54	95.35	2.66

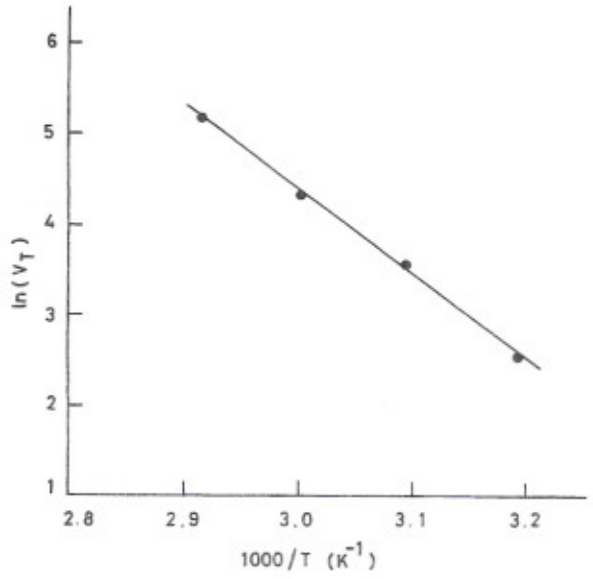

Figure 4. Plot of ln V_G versus 1000/T (K^{-1}) for unannealed Trifol-TN (etched in 6.0 N NaOH) for ^{238}U (17.17 MeV u^{-1}) ions.

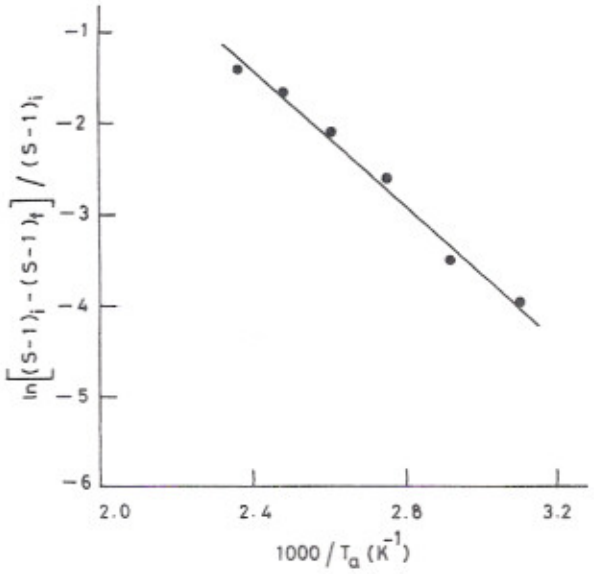

Figure 5. Variation of ln$[(S-1)_i - (S-1)_f]/(S-1)_i$ versus $1/T_a$ (10^3 K^{-1}) for annealing of tracks of ^{238}U (17.17 MeV u^{-1}) ions in Trifol-TN (etched in 6.0 N NaOH at 60 °C).

etching. The activation energy for bulk etching, E_G, is found to be 0.80 eV. The activation energies for track etching, E_T, for ^{238}U ions of energies 17.17 and 16.34 MeV u^{-1} are found to be nearly equal, i.e. 0.74 and 0.73 eV.

For annealed samples all etching parameters change after annealing at temperatures of 50, 70, 90, 110, 130 and 150 °C. For annealed samples the bulk rate slightly decreases with increase in annealing temperature. From annealing studies, it can be seen from figures 1 and 2 that the track rate etch rate, V_T, decreases with the healing of latent tracks. The track registration sensitivity, S, and etching efficiency decrease with the healing of latent tracks. The track registration sensitivity, S, and etching efficiency decrease with the annealing of latent tracks (table 3). To obtain the activation energy for annealing of latent tracks, the data were fitted using equations (2) and (3). The values of activation energy, E_a, were obtained from the slopes of graphs (figures 5 and 6) for ^{238}U ions of energy 17.17 MeV u^{-1}. The determined values of activation energy for the annealing of ^{238}U ion tracks are 0.29 eV (table 4) for both 17.17 and 16.34 MeV u^{-1} energies. The concept of a single activation energy (Modgil and Virk 1985, Green *et al* 1985, Salamon *et al* 1986, Virk 1995) is vindicated in this investigation also.

5. Range measurement of ^{238}U ions in Trifol-TN

For this investigation, the irradiated samples of Trifol-TN were etched in 6.0 N NaOH solution at a constant temperature of 60 °C using a constant-temperature bath. Etching of the tracks was performed for short intervals of time until the tips of the tracks became round. After successive etching, the samples were washed under running water for a few minutes and then dried in the folds of tissue paper. The dried and etched samples were scanned

Table 4. Activation energy values for annealing of tracks of ^{238}U ions in Trifol-TN.

Ion	Energy (MeV u^{-1})	Activation energy of annealing (eV)	
		Price *et al* (1987) (equation (2))	Bhatia and Virk (1989) (equation (3))
^{238}U	16.34	0.31 ± 0.02	0.29 ± 0.03
^{238}U	17.17	0.29 ± 0.01	0.29 ± 0.02

Table 5. Comparison between experimental and theoretical range values for ^{238}U ions in Trifol-TN.

Energy (MeV u^{-1})	R_{exp} (μm)	$R_{theoretical}$ (μm)			
		Benton and Henke (1969)	Mukherjee and Nayak (1979)	TRIM-95 (Ziegler 1995)	SRIM-97 (Biersack and Ziegler 1997)
16.34	251.5 ± 3	237.59 (−5)	242.44 (−4)	272.30 (8)	275.45 (9)
17.17	262.4 ± 3	249.89 (−5)	254.89 (−3)	286.13 (9)	289.41 (10)

Figures in parentheses give percentage deviation of theoretical results from the experimental ones.

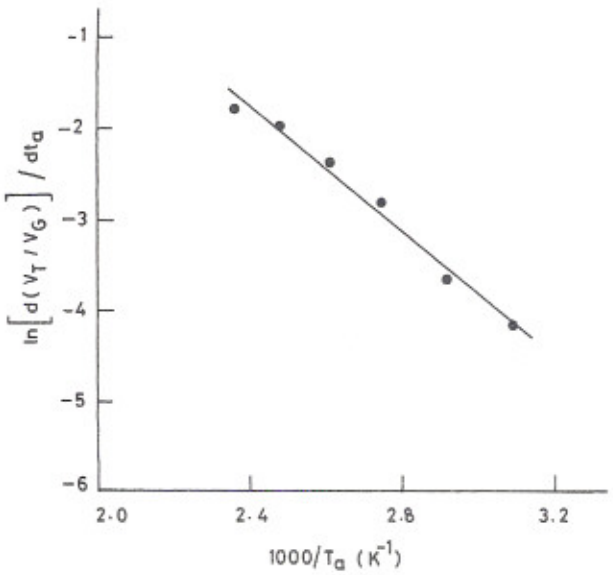

Figure 6. Variation of $\ln[d(V_T/V_G)/dt_a]$ versus $1/T_a$ (10^3 K^{-1}) for annealing of tracks of ^{238}U (17.17 MeV u^{-1}) ions in Trifol-TN (etched in 6.0 N NaOH at 60 °C).

at a magnification of 600×. After measuring the projected track length, the total etchable range was determined by applying the corrections due to bulk etching and over-etching (Dwivedi and Mukherjee 1979). This total etchable range is taken as the range of ^{238}U ions in Trifol-TN. The experimental range values have been compared with the theoretical range values from the Benton and Henke (1969), Mukherjee and Nayak (1979) and Ziegler *et al* (1985) formulations (table 5). TRIM-95 (Ziegler 1995) and SRIM-97 (Biersack and Ziegler 1997) based on the Ziegler *et al* (1985) formulation are found to overestimate the experimental range values while the Mukherjee and Nayak (1979) and Benton and Henke (1969) formulations underestimate the experimental data.

6. Conclusions

(i) The sensitivity of Trifol-TN to ^{238}U ions remains almost constant with the increase of etchant temperature.

(ii) Price *et al* (1987b) and Bhatia and Virk (1989) formulations (both) can be used to explain the annealing kinetics of radiation damaged Trifol-TN plastic. The determined value of activation energy for annealing of heavy ion tracks is ~0.29 eV.

(iii) The theoretical range value computed from TRIM-95 and SRIM-97 based on the Ziegler *et al* (1985) formulation overestimates the experimental range values by 10 per cent while the Mukherjee and Nayak (1979) and Benton and Henke (1969) formulations underestimate the experimental results by 5 per cent.

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