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Study on behaviour of pesticide Dimehypo in soil

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Abstract Degradation, adsorption and field fate of pesticide Dimehypo have been investigated. The results are as follows: hydrolysis of Dimehypo is very slow under pH range of 3 to 9. Degradation of Dimehypo in soil is mainly microorganism-related. Furthermore, Dimehypo and Nereistoxin can be rapidly degraded under ultraviolet light. Adsorption of Dimehypo by soil is negligible, while Nereistoxin can be sorbed to a large extent. After foliar spray in the rice field, distribution of Dimehypo concentration has the following sequence: crop > field water > soil. Field trials have proved considerable tendency of pesticide to leach down the profile, particular attention should be paid to threats of Dimehypo posed to the groundwater.
Keywords: Dimehypo; Nereistoxin; degradation; adsorption; leaching.

BACKGROUND

Dimehypo [2-(N, N-dimethylamino)-1, 3-(dithiolsulfonate sodium) propane] is a biomimetic insecticide. It is a derivative of Nereistoxin [4-(N, N-dimethylamino)-1, 2-dithiolane], which was isolated from a marine annelid, *Lumbriconereis Heteropoda Marenz*. In 1967, Padan was originally synthesized as one of the derivatives of Nereistoxin and developed into an insecticide by Takeda Chemical Industries in Japan (Shi, 1976; Guizhou Chemical Industries, 1980). Dimehypo is a intermediate chemical in the process of Padan synthesis and was developed as a novel insecticide in 1976 by Guiyang Chemical Industries in China. After application trials over more than twenty provinces, Dimehypo has been found to be effective against economically detrimental insects which attack a wide range of crops such as rice, wheat, vegetables and fruit trees (Tang, 1982; 1984). Now it is one of the most popular pesticides in China. Investigation data showed that area of Dimehypo application has steadily increased since the prohibition of organochlorine insecticides. Dimehypo is the most widely used pesticide in Jiangxi Province and application area comes second after Methamidophos in Zhejiang Province.

In 1970s, Guiyang Agricultural College and Jiangsu Agricultural College have separately published a few reports about the environmental effect of Dimehypo. The research work on environmental behavior of Dimehypo was still listed, after assessment, as a national key research program in "Seventh Five-Year Plan" construction period (1986 – 1990), for Dimehypo has been used popularly over ten years in China and has been exported to some southeastern countries in recent years. This study is a part of the research program and deals mainly with the behavior of Dimehypo in soil.

MATERIALS AND METHOD

Soil sampling, treatment and property determination

Five typical kinds of soil across China, i. e. black soil, meadow soil, paddy soil, yellow brown soil and red soil, were selected as the materials for laboratory experiments. Apart from paddy soil, the other four kinds were sampled in uncultivated land. The sampling depth was 0–20 cm and no Nereistoxin-related pesticides had been applied to all the sampling sites. All kinds of soil were treated and the physicochemical properties were determined by routine methods (Institute of Soil Science, 1978; Xiong, 1985), the results are shown in Table 1.

Table 1 Soil properties

Items	Black soil (Beian, Heilongjiang)	Meadow soil (Fengqiu, Henan)	Paddy soil (Jiangning, Jiangsu)	Yellow brown soil (Jiangning, Jiangsu)	Red soil (Yingtan Jiangxi)
OM, %	6.50	0.65	1.63	1.53	1.16
pH, 1:1	5.54	8.25	7.45	7.03	4.85
CEC, meq/100g	33.82	5.98	18.72	17.24	9.82
Sand, %	28.0	51.1	23.7	35.0	26.0
Silt, %	38.9	31.0	44.2	38.3	32.6
Clay, %	33.1	17.9	32.1	36.7	41.4
Fe_2O_3*, %	0.31	0.062	0.32	0.20	0.41
Al_2O_3*, %	0.26	0.065	0.14	0.12	0.24
MnO*, %	0.047	0.020	0.028	0.050	0.012
SiO_2*, %	0.053	0.064	0.11	0.10	0.031
Fe_2O_3**, %	1.33	1.02	1.65	1.96	3.92
SiO_2***, %	2.69	0.98	1.37	2.06	2.77
Al_2O_3***, %	0.68	0.091	0.30	0.34	1.38

* extracted by Tamm's solution ** extracted by DCB solution

*** extracted by 0.5 mol/L NaOH solution

Pesticide standards and reagents

Dimehypo and Nereistoxin hydrogen oxalate: analytical standard (above 99.5% purity) obtained from Guizhou Chemical Industries.

Methanol, hydrochloric acid, sodium chloride, sodium sulphide, anhydrous sodium sulfate: analytical grade. Methanol is distilled and there is no interference peak in the determination of Nereistoxin by gas chromatography.

Apparatus

Shimadzu gas chromatograph GC-9A equipped with a ^{63}Ni electron capture detector, C-R3A Chromatopac.

Thermostatic room, rotary photolysis apparatus, shaker, autoclave, water-bath, centrifuger, pH-meter, and routine glasswares.

Dimehypo residue determination of samples

Because of its large water solubility, Dimehypo can not be determined directly by the sensitive ECD. In the presence of sodium sulphide, Dimehypo could be changed quantitatively to Nereistoxin, which can be extracted by methanol in alkaline condition. After purification, Nereistoxin is measured by GC-ECD and the appropriate concentration of Dimehypo is calculated. For this method, the minimum detection limit of Dimehypo in water is 1 ppb, and variance value is less than 5%.

RESULTS AND DISCUSSIONS

Degradation of Dimehypo

1. Hydrolysis of Dimehypo

Hydrolysis of organic chemicals is important in the evaluation of environmental effect. In accordance with the procedures of OECD-Chemicals Testing Guidelines, the hydrolysis rates of Dimehypo in buffer solution of pH 3, 7 and 9 for five days were measured at 50 ℃ water-bath (lightproof). The results show that changes in Dimehypo concentration are less than 10% under these conditions. This means that hydrolysis of Dimehypo is very slow. Moreover, the half-life value calculated by extrapolation is more than one year.

As alkalinity of medium increased, hydrolysis of Dimehypo becomes strong. Dimehypo (the initial concentration was 20 ppm) was added to 0.01 mol/L NaOH (pH = 11.9) and 0.02 mol/L NaOH (pH = 12.3) to examine its hydrolysis at 50 ℃ water-bath, and first-order half-lives were calculated (Fig. 1). As judged by molecular structures and chemical properties of

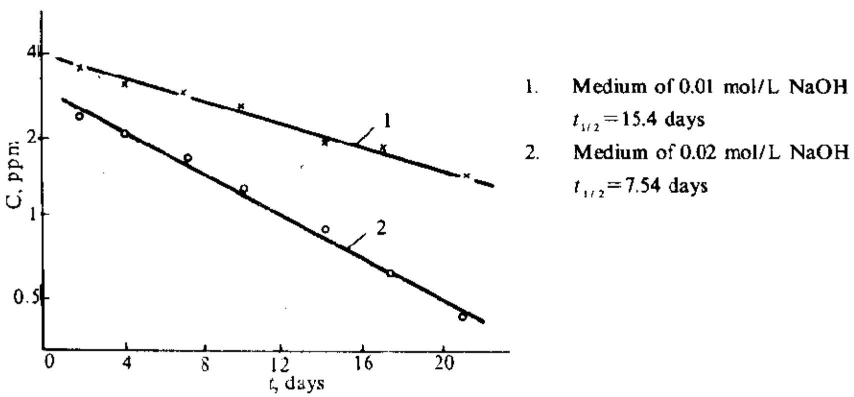
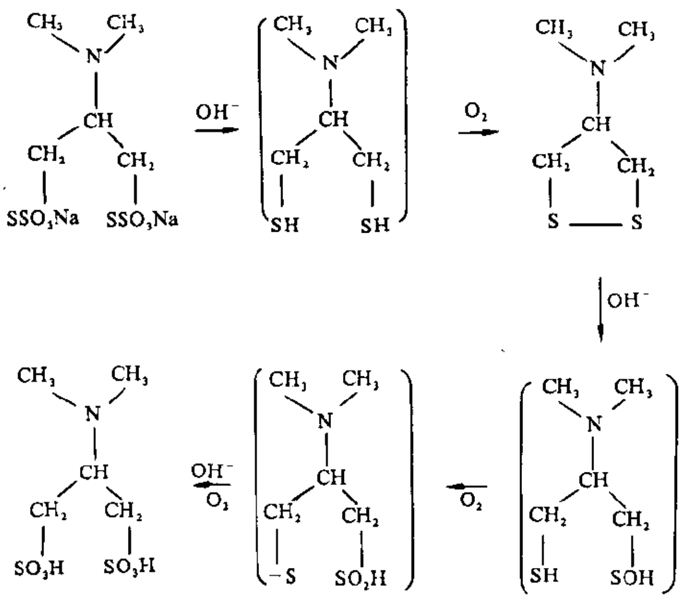


Fig. 1 Hydrolysis of Dimehypo

Dimehypo, it can, under alkaline and oxidative conditions, be transformed to Nereistoxin, which might be further decomposed.

The possible mechanism is shown as follows:



Asahi, Y. and Yoshida, T. (1977) have studied the hydrolysis dynamics of Padan and Nereistoxin, and the half-lives of Nereistoxin hydrolysis (measured by polarographic analysis) in different pH solutions are listed in Table 2.

Talbe 2 The half-lives of Nereistoxin solutions, 0.5mmol/L

Temperature, ℃	pOH	pH	Medium type	$t_{1/2}$
100	1.1	12.9	0.08 mol/L NaOH	2.2 h
	1.7	12.3	0.02 mol/L NaOH	7.9 h
	3.3	10.0	0.08 mol/L borate	20 h
	5.3	7.0	0.08 mol/L phosphate	26 h
	8.2	4.1	0.08 mol/L acetate	>100 h*
	11.2	1.1	0.08 mol/L HCl	>100 h*
50	1.1	12.9	0.08 mol/L NaOH	29 h
47	6.4	7.0	0.08 mol/L phosphate	95 d*
25	7.0	7.0	0.08 mol/L phosphate	880 d**

* no difference in 24 hours   ** calculated by extrapolation

It is manifested that half-lives of Nereistoxin are about 880 days (at pH 7, 25 ℃) and 96 days (at pH 6.4, 47 °C). This indicates that Nereistoxin is a stable compound, and its hydrolysis at natural pH conditions is very slow. While under the conditions of higher temperature and strong alkalinity, its hydrolysis rate becomes much faster. For example, the half-lives are 29 hours (at pOH 1.1, 50 °C) and 2.2 hours (at pOH 1.1, 100 °C), These results coincide quite well with the hydrolysis behavior of Dimehypo. Since Dimehypo can be easily transformed to Nereistoxin at alkaline conditions, it is proposed that the controlling factors of Dimehypo hydrolysis rate are not the process of Dimehypo transformation to Nereistoxin, but the step of further Nereistoxin decomposition.

2. Degradation of Dimehypo in soils

Red soil, black soil, meadow soil and yellow brown soil were selected as experimental materials for the degradation of Dimehypo in soil. The procedures can be listed as follows: weigh 50 g of soil into 150 ml flask, add distilled water to make soil moisture 60% of the maximum field capacity, record the total weight (flask+soil+water), and cork the flask with cotton. After two weeks of pre-incubation at 30 °C, fortify every flask with 2 ml Dimehypo of 100 ppm, place flasks in the thermostatic room at 30 ℃, add water every three days to maintain soil moisture at the designated level, and determine the concentration of Dimehypo in soil at intervals. The results at expressed by the relationsip of $c-t$ (Fig. 2) and the first order half-lives for Dimehypo degradations in soil are calculated (Table 3).

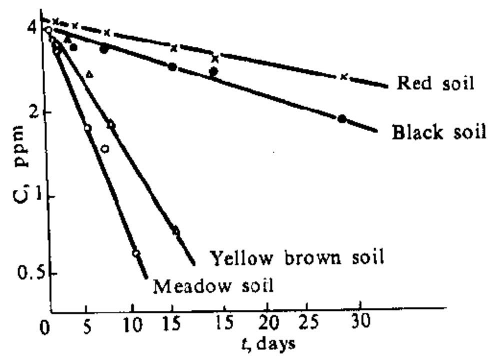


Fig. 2 Degradation of Dimehypo in soil

There are marked difference in persistence of Dimehypo in red soil, black soil, yellow brown soil and meadow soil, with the values of $t_{1/2}$ 69.3, 38.5, 6.0 and 4.10 days, respectively. This indicates that $t_{1/2}$ is related to the composition and property of soil, and it is found that $t_{1/2}$ is significantly correlated with soil pH value (the regression coefficient $r=-0.976^*$) among the soil properties listed in Table 1.

After autoclaving of the four kinds of soil, Dimehypo was added to soil for observing the effect of sterilization on the rate of breakdown. The results show that degradation of Dimehypo in sterilized soil is very slow and amount of degradation is less than 10% in 35 days. The calculated values of $t_{1/2}$ by extrapolation are several years, which is much longer than the situation of untreated soils. Dimehypo is very stable even in the treated meadow soil of pH 8.25. The comparison on persistence illustrates that Dimehypo degradation is related to biochemistry reaction of soil microorganisms.

In order to compare the degradation of dimehypo in upland and flooded soil, upland (adjusting the soil moisture to 60% of the maximum field capacity) and saturated (submerged in water) situations were simulated. The treatments were incubated in the thermostatic room at 30 °C for 50 days and sampled at the appropriate times. The $t_{1/2}$ is 5.0 days and 12.8 days separately for aerobic and anaerobic simulation, with the difference of more than two times (Fig. 3). This means the aerobic situation is conducive to the degradation of Dimehypo.

3. Photolysis of Dimehypo and Nereistoxin

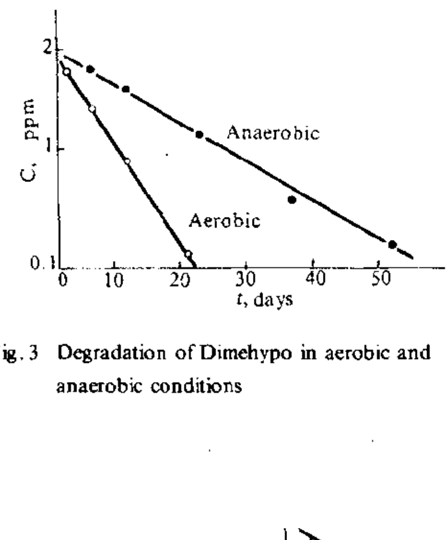


Fig. 3 Degradation of Dimehypo in aerobic and anaerobic conditions

The experiments were carried out in the rotary photolysis apparatus. The light source was 450 W middle pressure mercury lamp with 365 nm filter. Quartz tubes with solutions of Dimehypo or Nereistoxin were placed in the inner parts of rotary photolysis apparatus, and the tubes were kept at a distance of 163 mm to the light source. Solutions were sampled at intervals and photolysis rates were calculated. The results are expressed by ln C-t relationship and the first-order half-lives for photolysis are calculated (Fig. 4).

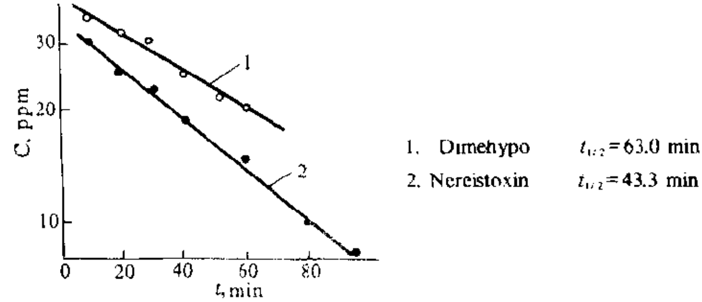
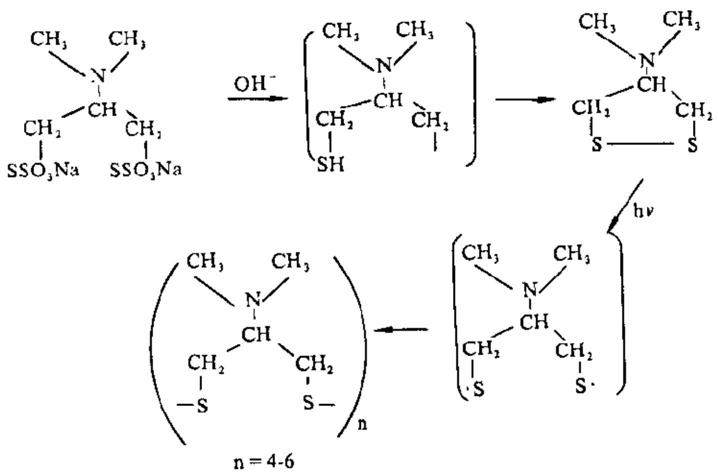


Fig. 4 Photolysis of Dimehypo and Nereistoxin under 365 nm ultraviolet light

Table 3 Calculated constants and correlation coefficients for Dimehypo degradation in soil (using equation ln $C = Ka + t$)

	Red soil	Black soil	Yellow brown soil	Meadow soil
a	1.328	1.367	1.516	1.440
k	0.0133	0.0180	0.116	0.169
r	0.982	0.978	0.983	0.989
$t_{1/2}$, d	69.3	38.5	6.0	4.10

There were reports about photolysis and photolytic products with Nereistoxin and Padan. From the results of infrared spectroscopy, ultraviolet spectroscopy, element analysis and mass spectroscopy experiments, Obayashi and Asaka believed that polymer of Nereistoxin (NTX-polymer) was formed after Nereistoxin absorbed photon. Following the photolysis of Dimehypo to Nereistoxin, similar NTX-polymer are probably formed. The possible mechanism is proposed as follows:



Adsorption of Dimehypo and Nereistoxin

Adsorption of Dimehypo and Nereistoxin in red soil, black soil, yellow brown soil, meadow soil and paddy soil were studied by batch equilibrium technique. The organic chemicals were dissolved in 0.01 mol/L $CaCl_2$ solution, and the soil/solution ratio was 1: 5. The equilibria were reached by shaking for 18 hours at 25℃.

The concentration of Dimehypo or Nereistoxin in solution and in soil were fitted to

Table 4 Adsorption parameters of Dimehypo and Nereistoxin in soils

	Parameter	Black soil	Meadow soil	Paddy soil	Yellow brown soil	Red soil
Dimehypo	K_f	1.04	0.834	0.770	0.930	0.533
	K_{oc}	27.6	221	81.5	105	79.2
	$1/n$	0.70	0.83	0.72	0.75	0.53
	r	0.990	0.997	0.999	0.999	0.984
Nereistoxin	K_f	54.4	2.74	9.86	9.69	7.22
	K_{oc}	1400	727	1043	1092	1072
	$1/n$	0.97	0.57	0.81	0.67	0.83
	r	0.977	0.987	0.998	0.999	0.996

Freundlich equation. Adsorption parameters such as K_f, $1/n$ and r, derived from Freundlich equation by least square method, are presented in Table 4.

Because soil colloids are usually negatively charged, they repel anionic Dimehypo molecule. So the amount of Dimehypo sorbed in soil is small. On the contrary, adsorption of Nereistoxin is relatively strong. There is a large difference in the extent of adsorption among different kinds of soil. This is especially manifested between black soil and meadow soil. Linear regression equation is used to analyze the relationship between adsorption coefficient and individual soil properties, it is found that K_f of Nereistoxin is significantly correlated to soil organic matter (r=1.000***). This means Nereistoxin, as an un-ionized material, is mainly sorbed in soil organic matter by hydrophobic bonding and Ver der Wall attraction.

K_{OC} is Freundlich K_f constant on the basis of organic carbon content of the soil (Table 4). The special contribution of soil organic matter to Nereistoxin adsorption, K_{OC} is more nearly constant than K_f for a range of soil and could better represent the adsorption capacity of Nereistoxin in soil.

Stepwise multiple linear regression analysis is employed to develop regression models for the chemicals, and two equations are as follows:

For Dimehypo:

$$K_f = 0.8693 + 8.0683\ (\text{active Mn}) - 1.5028\ (\text{active Si}) - 0.0977\ (\text{free Fe}) \qquad R^2 = 0.9999^{***}$$

For Nereistoxin:

$$K_f = 0.4158 + 8.7008\ (\text{OM}) - 0.1098\ (\text{Silt}) + 0.0739\ (\text{free Fe}) \qquad R^2 = 0.9999^{***}$$

It is noted that Tamm's solution-extractable active Mn, active Si and DCB solution-extractable free Fe are closely related to the adsorption of Dimehypo, and active Mn plays the most important role. It is proposed that metal-ion-bridged mechanism might be the principal one for Dimehypo adsorption, as Dimehypo is anionic in solution.

Fate of pesticide Dimehypo in paddy field

Field plot experiment was conducted in the rice field near Nanjing during 1988－1989. The pesticide Dimehypo was applied in the tillering rice, then soil, field water and crop were sampled and determined at intervals. The results show that foliar spray applied-Dimehypo will distribute among rice, field water and soil, and distribution concentration are determined by environmental conditions of application. Dimehypo concentration of crop is comparatively high and decreases with the lapse of time, and the total disappearance time is about 20 days; Dimehypo concentration of field water is in the range of ppm.

As to the chemical and biological characteristics of Dimehypo, Dimehypo in field water might decrease by photolysis, leaching and runoff; disappearance pathways in soil are leaching and biological breakdown; moreover, crop analysis results of Dimehypo and Nereistoxin show that once crop comes into contact with pesticide, Dimehypo is readily transformed to Nereistoxin, and further disappearance of Nereistoxin lies in the biological metabolism.

For the large water solubility and little adsorption, the leaching of Dimehypo is well worth of notice. 3.75 kg/ha of Dimehypo of aqueous solution (25%)was applied to 0.47 ha experimental paddy field on August 4, 1988, just like the normal practice to control rice insects. Soil from six sites (*A-F*) were sampled by auger in the field on October 12. Eight layers were separated for the sites with every layer of 10 cm, then the soil samples were analyzed for the total amount of Dimehypo and Nereistoxin (for reason of easy manipulation).

Table 5 illustrates that the pesticide can leach easily to subsoil, where it is resistant to further breakdown. Most of the layers in sampling site *B* have concentration over 50 ppb of total residue, with 89.4 ppb at the layer of 40－50cm. All other sampling sites except site *C* have been detected the presence of pesticide and its degradation product, and the overall detection rate is 69%. Because of the shallow groundwater table in the paddy field, it is worthy of particular attention of the leaching of Dimehypo and potential groundwater contamination.

Table 5 Concentrations of total residue of Dimehypo and Nereistoxin in soil profiles, ppb

Depth, cm	*A*	*B*	*C*	*D*	*E*	*F*
0－10	23.7	45.0	N.D.	N.D.	2.4	42.9
10－20	22.9	55.2	N.D.	1.8	21.4	35.1
20－30	20.0	55.4	N.D.	N.D.	5.4	30.7
30－40	11.2	60.5	N.D.	N.D.	6.6	20.5
40－50	N.D.	89.4	N.D.	1.0	0.9	12.4
50－60	N.D.	32.2	N.D.	5.9	N.D.	3.7
60－70	4.3	42.7	N.D.	4.1	5.4	2.4
70－80	N.D.	51.9	N.D.	N.D.	6.8	2.7

SUMMARY

The hydrolysis rate of Dimehypo is less than 10% at 50 °C in buffer solution of pH 3, 7 and 9. Under strong alkaline condition, Dimehypo can be easily changed to Nereistoxin. The degradation rate of Dimehypo in red soil, black soil, yellow brown soil and meadow soil slows down with the decrease of soil pH value. Furthermore, the disappearance of Dimehypo in soil is mainly a microorganisms-related process. Dimehypo and Nereistoxin are unstable under ultraviolet light exposure (450 W middle pressure mercury lamp, 365 nm filter).

Adsorption of Dimehypo by soils is negligible. On the contrary, Nereistoxin can be sorbed in soils to large extent. On the basis of the molecular structure and the experimental results, we suggest that metal-ion-bridged (especially $Mn^{2+,4+}$) mechanism might be the dominant interaction mechanism for Dimehypo and soil organic matter the main adsorption site for Nereistoxin.

Dimehypo applied in vigorous rice growth periods can be readily transformed to Nereistoxin in the crop body and disappears in about 20 days by further metabolism. There is no pesticide residue in brown rice. Considering the characteristics of Dimehypo (large water solubility, resistance to hydrolysis, little adsorption in soils, low degradation rate under normal soil pH value) and weak microbial activity in subsoil, particular attention should be paid to the leaching of Dimehypo and threats to groundwater contamination. Field experiment has proved the considerable potential of Dimehypo and Nereistoxin to leach down the profile in the paddy field.

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