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Variation in the Molecular Weight Distribution of Polyvinylpyrrolidone by Ball-Milling

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Variation in the molecular weight distribution of polyvinylpyrrolidone (PVP) by ball-milling in various kinds of atmosphere in the absence and in the presence of various kinds of organic and inorganic additives was investigated.

A line broken at several points was obtained by the logarithmic plot of $-\log R$ *versus* the molecular weight of PVP, M_u, and equation (1) was applied in the limited range of M_u, respectively, where R was the ratio of the weight of the polymers of molecular weight above M_u to the total weight of the polymers, and k and n were parameters dependent on the experimental conditions and so on.

$$R = \exp(-kM_u^n) \qquad (1)$$

The existence of the critical molecular weight, M_c, was observed, at the region of M_u below which n was larger than 1.0 and formation of the polymers of M_u below M_c was considered to become more difficult with a decrease of M_u. The value of M_c was below 4×10^5 and varied remarkably by the kind of the additive and by the ball-milling atmosphere.

Theoretical consideration was made on the molecular weight distribution of the polymers formed by chain scission of polymers by application of the mechanical stress, by assuming that chain scission was produced by activation of the bonds between atoms of the main chain by the mechanical stress and that these activated bonds were distributed at random and obeyed to Poisson's distribution law. It was suggested from the consideration mentioned above and from the investigation of the value of n in equation (1) and of the variation of R with the ball-milling time that, in many cases, random chain scission was most probable and that the density of the activated bonds over a polymer of low molecular weight was approximately equal to or higher than the density over a polymer of high molecular weight.

Keywords——organic and inorganic additives; ball-milling atmosphere; Poisson's distribution law; the mean density of the activated bonds over a polymer, γ; the critical molecular weight, M_c; the parameter n in equation (11); the parameters, γ_1 and γ_2 in equation (17); random chain scission

In the previous papers, polyvinylpyrrolidone (PVP) was ball-milled in various kinds of atmosphere in the presence of various kinds of organic and inorganic additives, and it was clarified that a decrease of molecular weight of PVP by ball-milling was influenced by the presence of the additive or by the ball-milling atmosphere.[2,3]

In this paper, variation in the molecular weight distribution of PVP by ball-milling was investigated, and dependence of the variation on the presence of the additive or the ball-milling atmosphere was discussed.

Theoretical

It is well known that Rosin-Rammler's law expressed by equation (1) applies well to the particle size distribution of the crushed powders, where R is the ratio of the weight of

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[1] Location: *Hatanodai 1-5-8, Shinagawa-ku, Tokyo.*

[2] N. Kaneniwa and A. Ikekawa, *Chem. Pharm. Bull.* (Tokyo), **21**, 1539 (1973).

[3] N. Kaneniwa and A. Ikekawa, *Chem. Pharm. Bull.* (Tokyo), **25**, 1534 (1977).

the particles of the size above x to the total weight of the particles, x_e is the particle size for which R is equal to $1/e$, and k and n are the parameters dependent on the ball-milling condition and so on.[4,5]

$$R = \exp(-kx^n) = \exp\{-(x/x_e)^n\} \tag{1}$$

Equation (1) is expressed by equation (2), when n is equal to 1.0.

$$R = \exp(-kx) = \exp\{-(x/x_e)\} \tag{2}$$

Gilvarry obtained equation (2) theoretically on the basis of the assumption that fracture of brittle solids was produced by activation of the flaws or cracks existent in a solid prior to application of the stress system, and that these activated points were distributed at random and obeyed to Poisson's distribution law.[6]

Here, it is assumed that chain scission is produced by activation of a part of the bonds between atoms of the main chains by application of the mechanical stress to the polymers. It is also assumed that these activated bonds are distributed at random, that the density of the activated bonds over a polymer molecule is extremely small and that the activated bonds conform to Poisson's distribution law. By application of Gilvarry's discussion to the scission of the chains of the polymers by the mechanical stress under the assumptions mentioned above, equation (3) is obtained, where $W(M)$ is the cumulative weight of the fragments with molecular weight up to M produced by applying mechanical stress to a polymer of the weight of W_0, and γ repersents the mean density of the activated bonds over a polymer molecule.[6]

$$1 - W(M)/W_0 = e^{-\gamma M} \tag{3}$$

On the other hand, equation (4) is obtained by substituting M for x in equation (1).

$$R = \exp(-kM^n) = \exp\{-(M/M_e)^n\} \tag{4}$$

In equation (4), R is the ratio of the cumulative weight of the fractions of molecular weight above M to the total weight of the polymers, and M_e is the molecular weight for which R is equal to $1/e$. Equation (4) is identical with equation (3), if n is equal to 1.0 and γ is equal to $1/M_e$.

In the actual case, many polymer molecules of a wide molecular weight distribution are treated mechanically at the same time. Now, M_i is the molecular weight of the polymers of the i th fraction obtained by fractionating the original polymers according to the molecular weight. The mean density of the activated bonds over a polymer is expressed as a function of M_i, $\gamma(M_i)$, if the mean density depends on the molecular weight of the original polymer, though they are distributed at random on one polymer. In this case, equation (5) is applied, where ϕ_{M_i} is the number of moles of the polymers of the molecular weight of M_i in the original material.

$$R = 1 - W(M)/W_0 = \sum_i \phi_{M_i} M_i e^{-\gamma(M_i)\cdot M} / \sum_i \phi_{M_i} \cdot M_i \tag{5}$$

Results and Discussion

In the previous paper, the relation between molecular weight by viscometry, M_η, and intrinsic viscosity was obtained for the KH_2PO_4–Na_2HPO_4 buffer solution of PVP of M_η between 7.5×10^3 and 10^6, and in this paper, the value of M_η of PVP was obtained by viscometry using this relation.[7]

In the previous papers, PVP K90 was ball-milled in various kinds of atmosphere in the absence of the additive or in the presence of various kinds of organic or inorganic additives,

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4) K. Matsui, *Funsai*, No. 16, 68 (1971).
5) P.O. Rosin and E. Rammler, *Kolloid-Z.*, **67**, 16 (1934).
6) J.J. Gilvarry, *J. Appl. Phys.*, **32**, 391 (1961).
7) N. Kaneniwa and A. Ikekawa, *Chem. Pharm. Bull.* (Tokyo), **20**, 1536 (1972).

and a decrease of M_η by ball-milling was investigated.[2,3,7] These samples were fractionated by Sepharose 6B and the mean molecular weight of PVP in the i th fraction, $M_{\eta i}$, was measured, and the variation in the molecular weight distribution of PVP was investigated.

In case of ball-milling in air ,the peak in the molecular weight distribution curve shifted from the molecular weight of approximately 10^6 to lower molecular weight with the lapse of the ball-milling time in the presence of white alundum, *p*-hydroquinone or barbituric acid.[2] This tendency was also observed in the presence of the fine powders of activated charcoal. But in case of the addition of the other powders or in the absence of the additive, the original peak at the molecular weight around 10^6 decreased, a new peak appeared at the lower molecular weight and increased by ball-milling.[2]

The similar phenomenon was also observed in case of ball-milling in the atmosphere other than air, as shown in Fig. 1 and 2. In case of ball-milling in nitrogen in the presence of phenothiazine or ball-milling in the presence of chloranil in oxygen containing small quantity of the vapor of distilled water, the peak shifted from the molecular weight of approximately 10^6 to lower molecular weight with the lapse of the ball-milling time. But in the other cases, the peak at the molecular weight around 10^6 decreased, a new peak appeared at the lower molecular weight and increased by ball-milling. The above finding seems to suggest that there is a characteristic pattern in the way how the chains of PVP molecules are broken by ball-milling. Then, the variation of molecular weight of PVP by ball-milling was investigated.

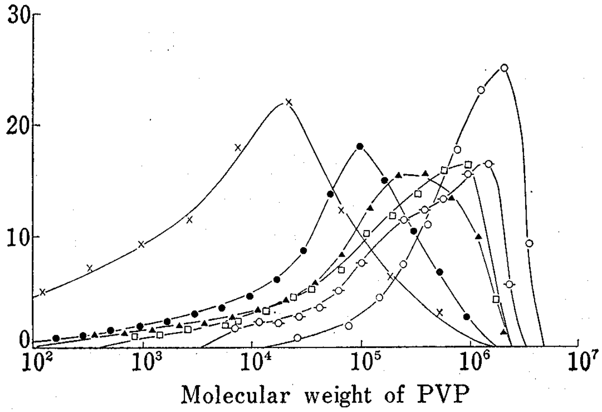

Fig. 1. Variation in Molecular Weight Distribution of PVP by Ball-Milling in Nitrogen in the Precense of 10 w/w % of Phenothiazine

$J_b=0.22$, $J_s=0.06$[3] (referred to Table I).
Ball-milling time (hr).
○, 0; -○-, 93; □, 115; ▲, 140; ●, 175; ×, 211.

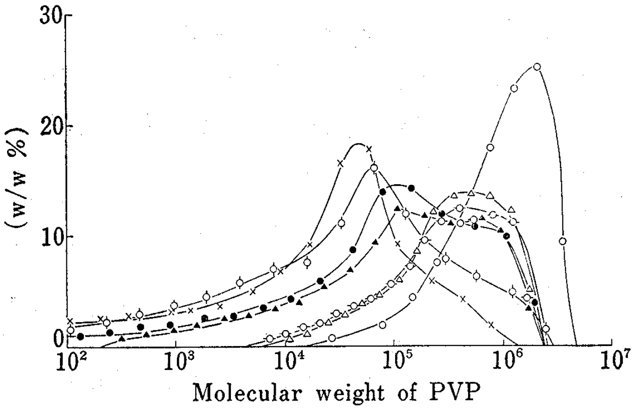

Fig. 2. Variation in Molecular Weight Distribution of PVP by Ball-Milling in Nitrogen in the Presence of 10 w/w % of Vitamin K_3

$J_b=0.22$, $J_s=0.06$[3] (referred to Table I).
Ball-milling time (hr).
○, 0; -○-, 125; △, 145; ▲, 166; ●, 189; ϕ, 222; ×, 251.

1) A Decrease of M_e by Ball-Milling

As shown in Fig. 3, a line broken at two or three points was obtained by the logarithmic plot of $-\log R$ *versus* M_u obtained by equation (6).

$$M_u = (M_{\eta i} \cdot M_{\eta i+1})^{1/2} \tag{6}$$
$$M_{\eta i} > M_{\eta i+1}$$

As shown in Fig. 4, M_e obtained by reading the value of M_u for R of $1/e$ on the $\log(-\log R)$ $-\log M_u$ line decreased gradually by ball-milling. In case of the addition of virtamin K_3, M_e was larger than M_η at the first stage and smaller than M_u at the last stage of ball-milling. (Fig. 5). The same tendency was also observed in case of the addition of zinc oxide, activated charcoal, talc or acridine, but this tendency was not so remarkable as the tendency in Fig. 5. In the other cases, M_e was identical or parallel to M_η, and the difference between them was small.

As shown in Fig. 6, equation (7) was applied to a decrease of M_e by ball-milling in the wide range of M_e, where t_{ie} was the induction period after the lapse of which M_e began to decrease, t was the ball-milling time, and k_{me} and β_e were the parameters dependent on the kind of the additive, ball-milling atmosphere and so on.

$$\begin{aligned} t \leq t_{ie} &\quad -dM_e/dt = 0 \\ t > t_{ie} &\quad -dM_e/dt = k_{me}M_e^{\beta_e} \end{aligned} \qquad (7)$$

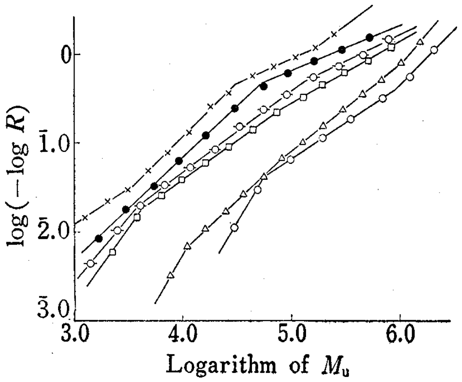

Fig. 3. Relation between R and M_u for PVP Ball-Milled in Nitrogen in the Presence of 10 v/v % of Talc

J_b=0.22, J_s=0.06[3] (referred to Table I).
Ball-milling time (hr).
○, 0; △, 72; □, 103; -○-, 133; ●, 169; ×, 201.

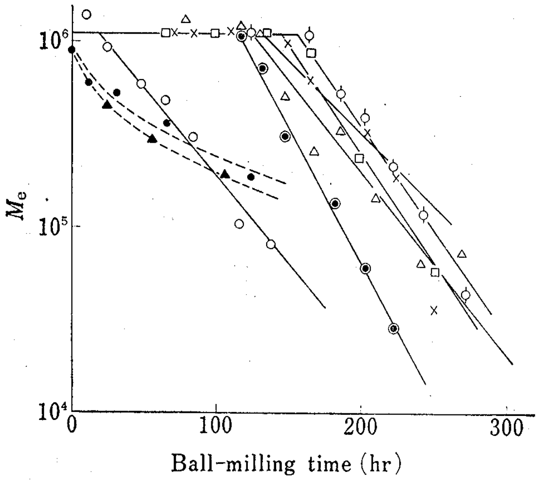

Fig. 4. Decrease of M_e of PVP by Ball-Milling in the Presence of Activated Charcoal (AC) in Various Kinds of Atmosphere

J_b=0.22, J_s=0.06[2,3] (referred to Table I).

	Kind of AC	Content of AC (w/w %)	Ball-milling atmosphere
●,	Absent		Nitrogen.
▲,	Absent		Air.
⊙,	Granules	10	$N_2(H_2O)$.
△,	Granules	10	$N_2(H_2O_2)$.
□,	Granules	15.1	Air.
○,	Fine powders	10	Air.
×,	Granules	15.1	Oxygen.
ȯ,	Granules	10	$O_2(H_2O)$.

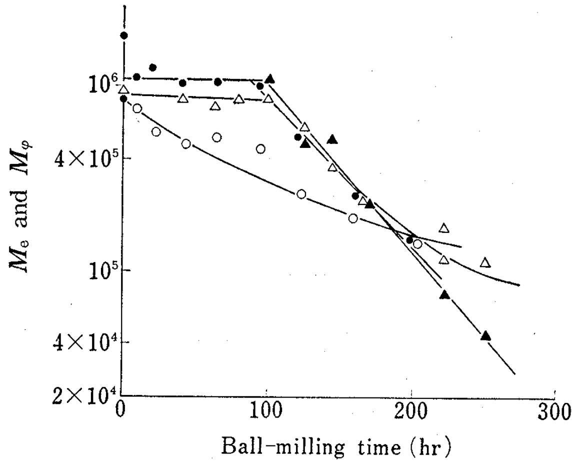

Fig. 5. Comparison of M_e with M_η for PVP Ball-Milled in the Presence of 10 w/w % of Vitamin K_3

J_b=0.22, J_s=0.06[2,3] (referred to Table I).

Ball-milling atmosphere	M_e	M_η
Nitrogen	▲	△
Air	●	○

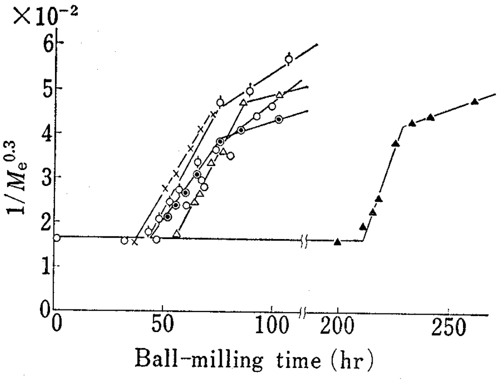

Fig. 6. Application of Equation (7) to a Decrease of M_e by Ball-Milling in the Presence of Chloranil in Various Kinds of Atmosphere

J_b=0.43, J_s=0.03[3] (referred to Table I).

	Weight content of chloranil (w/w %)	Ball-milling atmosphere
⊙,	5	$N_2(H_2O)$.
△,	5	$N_2(H_2O_2)$.
○,	5	Air.
▲,	10	Air.
×,	5	O_2.
ȯ,	5	$O_2(H_2O)$.

It was reported in the previous paper that the same relation as equation (7) was applied to a decrease of M_η by ball-milling, though the parameters t_i, M_η, k and β were in place of t_{ie}, M_e, k_{me} and β_e, respectively.[2] Table I, II, III and IV show the numerical values of the parameters β_e, t_{ie}, k_{me}, β, t_i and k. The values of β, t_i and k were quoted from the data in the previous papers.[2,3] In case of the addition of vitamin K_3, β_e was smaller than β, and this phenomenon seemed to be due to the fact in Fig. 5. In case of ball-milling in air in the presence of vitamin K_3, methylene blue or phenothiazine, t_{ie} was much larger than t_i. This fact suggests that the polymers of low molecular weight formed at the first stage of ball-milling largely influence on the viscosity of the aqueous solution of the ball-milled sample. But, in the other cases, the values of t_{ie} and β_e were similar to those of t_i and β, respectively. These facts seem to suggest that the values of molecular weight obtained by viscometry reported in the previous paper[7] are adequate, in spite of the wide range of molecular weight.

TABLE I. Numerical Values of β_e, t_{ie}, k_{me}, β, t_i and k for Ball-Milling of PVP in the Presence of 10 v/v % of Inorganic Additives

$J_b{}^{a)}=0.22$, $J_s{}^{b)}=0.06$[2,3,7]

Additive	Atmosphere	β_e	t_{ie}(hr)	k_{me}(hr^{-1})	β	t_i(hr)	k(hr^{-1})
Absent	Nitrogen	1.3	0	2.3×10^{-4}	1.3	0	3.0×10^{-4}
	Air	1.3	0	2.7×10^{-4}	1.0	0	1.6×10^{-2}
White alundum (type 40)	Nitrogen	1.6	0	3.9×10^{-5}	1.3	0	6.7×10^{-4}
	Air	1.4	0	1.3×10^{-3}	1.5	0	5.9×10^{-5}
Silica sands (type 3)	Nitrogen	1.0	0	2.4×10^{-2}	1.3	0	3.1×10^{-4}
	Air	1.5	0	3.6×10^{-5}	1.9	0	4.7×10^{-7}
Zinc oxide	Nitrogen	1.0	38	2.1×10^{-2}	1.4	35	9.3×10^{-5}
	Air	1.5	55	4.9×10^{-5}	1.5	40	2.6×10^{-5}
Barium sulfate	Air	1.3	34	6.1×10^{-4}	1.4	0	1.0×10^{-4}
Sodium chloride	Nitrogen	1.3	30	6.1×10^{-4}	1.3	0	3.3×10^{-4}
	Air	1.3	32	8.3×10^{-4}	1.2	12	2.0×10^{-3}
Granules of activated charcoal	Air	1.0	152	2.5×10^{-2}	1.0	147	2.4×10^{-2}
Talc	Nitrogen	1.3	42	6.3×10^{-4}	1.4	24	2.1×10^{-4}
	Air	1.0	66	2.6×10^{-2}	1.0	30	1.6×10^{-2}

a) The ratio of the apparent volume of balls in the mill to the capacity of the mill.
b) The ratio of the apparent volume of the samples in loose packing in the mill to the capacity of the mill.

TABLE II. Numerical Values of β_e, t_{ie}, k_{me}, β, t_i and k for Ball-Milling of PVP in the Presence of 10 w/w % of Organic Additives

$J_b=0.22$, $J_s=0.06$[2,3] (referred to Table I)

Additive	Atmosphere	β_e	t_{ie}(hr)	k_{me}(hr^{-1})	β	t_i(hr)	k(hr^{-1})
Vitamin K_3	Nitrogen	1.0	103	2.0×10^{-2}	1.4	104	1.4×10^{-4}
	Air	1.0	90	1.9×10^{-2}	1.6	0	4.3×10^{-6}
Acridine	Nitrogen	1.0	112	2.2×10^{-2}	1.0	115	1.8×10^{-2}
	Air	1.0	28	2.2×10^{-2}	1.1	0	6.2×10^{-3}
Methylene blue	Air	1.0	60	3.1×10^{-2}	1.1	0	4.7×10^{-3}
Phenothiazine	Nitrogen	1.0	87	2.2×10^{-2}	0.74	70	5.0×10^{-1}
	Air	1.0	105	1.1×10^{-2}	1.0	40	9.4×10^{-3}
p-Hydroquinone	Nitrogen	1.0	0	1.7×10^{-2}	1.0	0	1.6×10^{-2}
	Air	1.5	0	4.1×10^{-5}	1.5	0	3.7×10^{-5}
Barbituric acid	Nitrogen	1.3	0	1.7×10^{-3}	1.4	0	2.1×10^{-4}
	Air	1.4	0	2.1×10^{-4}	1.5	0	6.6×10^{-5}

TABLE III. Numerical Values of β_e, t_{ie}, k_{me}, β, t_i and k for Ball-Milling PVP in the Presence of Activated Charcoal (AC) in Various Kinds of Atmosphere
$J_b=0.22$, $J_s=0.06^{2,3)}$ (referred to Table I)

Content of AC	Kind of AC	Atmosphere	β_e	t_{ie}(hr)	k_{me}(hr^{-1})	β	t_i(hr)	k(hr^{-1})
10% w/w	Granules	$N_2(H_2O)$[a]	1.0	116	3.4×10^{-2}	1.0	110	2.7×10^{-2}
10% w/w	Granules	$N_2(H_2O_2)$[a]	1.0	130	2.6×10^{-2}	1.0	107	1.7×10^{-2}
10% v/v[b]	Granules	Air	1.0	152	2.5×10^{-2}	1.0	147	2.6×10^{-2}
10% v/v[b]	Granules	O_2	1.0	142	2.2×10^{-2}	1.0	192	2.4×10^{-2}
10% w/w	Granules	$O_2(H_2O)$[a]	1.0	164	3.0×10^{-2}	2.0	167	1.0×10^{-7}
10% w/w	Fine powders	Air	1.0	26	2.4×10^{-2}	1.0	0	2.5×10^{-2}

a) $N_2(H_2O)$, in nitrogen containing the vapor of distilled water with the vapor pressure of 17 mmHg;
$N_2(H_2O_2)$, in nitrogen containing the vapor of 30 w/w of the aqueous solution of hydrogen peroxide with the vapor pressure of 15 mmHg;
$O_2(H_2O)$, in oxygen containing the vapor of distilled water with the vapor pressure of 16 mmHg.
b) 10 v/v %=15.1 w/w %, (v/v % by true volume).

TABLE IV. Numerical Values of β_e, t_{ie}, k_{me}, β, t_i and k for Ball-Milling PVP in the Presence of Chloranil in Various Kinds of Atmosphere
$J_b=0.43$, $J_s=0.03^{3)}$ (referred to Table I)

Weight content of chloranil (%)	Atmosphere	β_e	t_{ie}(hr)	k_{me}(hr^{-1})[a]	β	t_i(hr)	k(hr^{-1})[b]
5	$N_2(H_2O)$[c]	1.2	44	2.2×10^{-3}	1.2	45	4.3×10^{-3}
5	$N_2(H_2O_2)$[c]	1.4	55	3.5×10^{-3}	1.1	56	3.8×10^{-3}
5	Air	1.2	55	3.5×10^{-3}	1.2	47	3.8×10^{-3}
5	O_2	1.5	39	2.9×10^{-3}	1.3	37	3.8×10^{-3}
5	$O_2(H_2O)$[c]	1.3	44	3.0×10^{-3}	1.3	37	3.8×10^{-3}
10	Air	1.2	209	4.4×10^{-3}	1.2	210	4.8×10^{-3}

a) The values of k_{me} are those for the case of the mean value of β_e of 1.30.
b) The values of k are those for the case of the mean value of β of 1.25.
c) $N_2(H_2O)$, in nitrogen containing the vapor of distilled water with the vapor pressure of 22 mmHg;
$N_2(H_2O_2)$, in nitrogen containing the vapor of 30 w/w % of the aqueous solution of hydrogen peroxide with the vapor pressure of 13 mmHg;
$O_2(H_2O)$, in Oxygen containing the vapor of distilled water with the vapor pressure of 22 mmHg.

TABLE V. Numerical Values of n for PVP Ball-Milled in the Absence of the Additive
$J_b=0.22$, $J_s=0.06^{7)}$ (referred to Table I)

Atmosphere								
Nitrogen			Air			Oxygen		
t	L	n	t	L	n	t	L	n
0	$1.2\times10^6\leq M_u$	1.2	21	$1.3\times10^6\leq M_u$	1.1	21	$1.2\times10^6\leq M_u$	1.0
	$5.2\times10^4\leq M_u\leq1.2\times10^6$	0.86		$4.2\times10^4\leq M_u\leq1.3\times10^6$	0.63		$4.2\times10^4\leq M_u\leq1.2\times10^6$	0.65
	$M_u\leq5.2\times10^4$	1.9		$M_u\leq4.2\times10^4$	1.6		$M_u\leq4.2\times10^4$	1.4
11	$1.2\times10^6\leq M_u$	1.1	54	$1.2\times10^6\leq M_u$	0.84	54	$1.2\times10^6\leq M_u$	0.84
	$4.1\times10^4\leq M_u\leq1.2\times10^6$	0.76		$3.4\times10^4\leq M_u\leq1.2\times10^6$	0.57		$4.2\times10^4\leq M_u\leq1.2\times10^6$	0.55
	$M_u\leq4.1\times10^4$	1.4		$M_u\leq3.4\times10^4$	1.9		$M_u\leq4.2\times10^4$	1.6
30	$10^6\leq M_u$	1.1	103	$1.2\times10^6\leq M_u$	0.64	100	$1.2\times10^6\leq M_u$	0.75
	$4.0\times10^4\leq M_u\leq 10^6$	0.71		$4.8\times10^4\leq M_u\leq1.2\times10^6$	0.48		$3.5\times10^4\leq M_u\leq1.2\times10^6$	0.46
	$M_u\leq4.0\times10^4$	1.4		$M_u\leq4.8\times10^4$	1.9		$M_u\leq3.5\times10^4$	2.0
67	$10^6\leq M_u$	0.96						
	$4.0\times10^4\leq M_u\leq 10^6$	0.51						
	$M_u\leq4.0\times10^4$	1.7						
123	$6.7\times10^5\leq M_u$	0.62						
	$3.8\times10^4\leq M_u\leq6.7\times10^5$	0.41						
	$M_u\leq3.8\times10^4$	1.6						

t; Ball-milling time (hr), L; The range of M_u.

TABLE VI. The Numerical Values of n for PVP Ball-Milled in the Presence of the Inorganic Additives

$J_b=0.22$, $J_s=0.06$[2,3] (referred to Table I)

Additive	Atmosphere					
	Nitrogen			Air		
	t	L	n	t	L	n
White alundum	9		0.69	7		0.98
	21		0.63	31	$1.2\times10^5\leqq M_u$	0.73
	46	$1.3\times10^4\leqq M_u$	0.73		$M_u\leqq1.2\times10^5$	1.1
		$M_u\leqq1.3\times10^4$	0.49	61	$10^5\leqq M_u$	0.83
	98	$10^5\leqq M_u$	0.66		$M_u\leqq 10^5$	1.1
		$1.1\times10^4\leqq M_u\leqq 10^5$	0.93	103		0.70
		$M_u\leqq1.1\times10^4$	0.61			
Silica sands	15	$3.6\times10^4\leqq M_u$	0.73	14	$3.4\times10^5\leqq M_u$	1.2
		$M_u\leqq3.6\times10^4$	1.3		$M_u\leqq3.4\times10^5$	1.7
	36	$3.5\times10^4\leqq M_u$	0.61	53	$9.1\times10^4\leqq M_u$	0.68
		$M_u\leqq3.5\times10^4$	1.4		$M_u\leqq9.1\times10^4$	1.5
	56	$2.4\times10^4\leqq M_u$	0.49	100	$9.5\times10^4\leqq M_u$	0.60
		$M_u\leqq2.4\times10^4$	1.4		$M_u\leqq9.5\times10^4$	1.4
	75	$4.2\times10^4\leqq M_u$	0.53	202	$8.5\times10^4\leqq M_u$	0.38
		$M_u\leqq4.2\times10^4$	1.6		$M_u\leqq8.5\times10^4$	1.8
	100	$3.3\times10^4\leqq M^n$	0.42			
		$M_u\leqq3.3\times10^4$	1.6			
	129	$2.0\times10^4\leqq M_u$	0.36			
		$M_u\leqq2.0\times10^4$	1.8			
	160	$2.0\times10^4\leqq M_u$	0.33			
		$M_u\leqq2.0\times10^4$	1.4			
	201	$7.0\times10^4\leqq M_u$	0.31			
		$M_u\leqq7.0\times10^4$	0.66			
Zinc oxide	15	$5.0\times10^4\leqq M_u$	0.87	59	$5.4\times10^4\leqq M_u$	0.99
		$M_u\leqq5.0\times10^4$	1.1		$M_u\leqq5.4\times10^4$	2.1
	36	$5.5\times10^4\leqq M_u$	1.2	80	$4.0\times10^4\leqq M_u$	0.89
		$M_u\leqq5.5\times10^4$	1.6		$M_u\leqq4.0\times10^4$	2.6
	56	$1.1\times10^5\leqq M_u$	1.1	106	$3.0\times10^4\leqq M_u$	0.63
		$M_u\leqq1.1\times10^5$	1.7		$M_u\leqq3.0\times10^4$	1.2
	75	$8.0\times10^4\leqq M_u$	0.78	172	$5.0\times10^4\leqq M_u$	0.44
		$M_u\leqq8.0\times10^4$	1.7		$M_u\leqq5.0\times10^4$	0.99
	100	$2.8\times10^4\leqq M_u$	0.47	201	$5.0\times10^4\leqq M_u$	0.44
		$M_u\leqq2.8\times10^4$	1.0		$M_u\leqq5.0\times10^4$	1.2
	129	$4.6\times10^4\leqq M_u$	0.55			
		$M_u\leqq4.6\times10^4$	1.6			
	160	$2.7\times10^4\leqq M_u$	0.43			
		$M_u\leqq2.7\times10^4$	1.4			
	201	$2.4\times10^4\leqq M_u$	0.40			
		$M_u\leqq2.4\times10^4$	1.5			
Barium sulfate	8	$1.1\times10^5\leqq M_u$	1.1			
		$M_u\leqq1.1\times10^5$	1.8			
	33	$7.0\times10^4\leqq M_u$	0.89			
		$M_u\leqq7.0\times10^4$	1.6			
	55	$7.0\times10^4\leqq M_u$	0.74			
		$M_u\leqq7.0\times10^4$	1.3			
	78	$6.4\times10^4\leqq M_u$	0.62			
		$M_u\leqq6.4\times10^4$	1.5			
	101	$8.6\times10^4\leqq M_u$	0.52			
		$M_u\leqq8.6\times10^4$	1.3			
	202	$4.0\times10^4\leqq M_u$	0.40			
		$M_u\leqq4.0\times10^4$	1.2			

Additive	Atmosphere					
	Nitrogen			Air		
	t	L	n	t	L	n
Sodium chloride	9	$1.3\times10^5\le M_u$	1.2	8	$8.0\times10^4\le M_u$	1.0
		$M_u\le1.3\times10^5$	1.7		$M_u\le8.0\times10^4$	2.0
	18	$2.0\times10^5\le M_u$	1.1	33	$7.2\times10^4\le M_u$	0.96
		$M_u\le2.0\times10^5$	1.5		$M_u\le7.2\times10^4$	2.2
	36	$2.0\times10^5\le M_u$	0.85	55	$7.0\times10^4\le M_u$	0.90
		$M_u\le2.0\times10^5$	1.0		$M_u\le7.0\times10^4$	1.8
	57	$7.0\times10^4\le M_u$	0.72	75	$5.0\times10^4\le M_u$	0.53
		$M_u\le7.0\times10^4$	1.0		$M_u\le5.0\times10^4$	1.2
	75	$8.0\times10^4\le M_u$	0.79	105	$5.0\times10^4\le M_u$	0.54
		$M_u\le8.0\times10^4$	1.6		$M_u\le5.0\times10^4$	1.4
	95	$9.0\times10^4\le M_u$	0.65	131	$4.8\times10^4\le M_u$	0.66
		$M_u\le9.0\times10^4$	1.2		$M_u\le4.8\times10^4$	1.6
	121	$5.0\times10^4\le M_u$	0.57	199	$2.5\times10^4\le M_u$	1.1
		$M_u\le5.0\times10^4$	2.1		$M_u\le2.5\times10^4$	3.0
	153	$1.1\times10^5\le M_u$	0.38			
		$4.0\times10^4\le M_u\le1.1\times10^5$	0.83			
		$M_u\le4.0\times10^4$	2.1			
	201	$3.5\times10^4\le M_u$	0.54			
		$1.6\times10^4\le M_u\le3.5\times10^4$	1.3			
		$M_u\le1.6\times10^4$	2.8			
Talc	72	$8.0\times10^4\le M_u$	0.99	72		0.86
		$M_u\le8.0\times10^4$	1.1			
	103	$6.0\times10^4\le M_u$	0.73	106	$10^4\le M_u$	0.56
		$M_u\le6.0\times10^4$	0.86		$M_u\le10^4$	1.3
	133	$8.0\times10^4\le M_u$	0.60	131	$1.2\times10^4\le M_u$	0.49
		$M_u\le8.0\times10^4$	0.96		$M_u\le1.2\times10^4$	1.4
	169	$5.0\times10^4\le M_u$	0.52	166	$1.3\times10^4\le M_u$	0.35
		$M_u\le5.0\times10^4$	1.1		$M_u\le1.3\times10^4$	1.2
	201	$4.3\times10^4\le M_u$	0.57	204	$1.9\times10^4\le M_u$	0.31
		$M_u\le4.3\times10^4$	1.1		$M_u\le1.9\times10^4$	1.2

TABEE VII. The Numerical Values of n for PVP Ball-Milled in the Presence of Organic Additives

$J_b=0.22$, $J_s=0.06$[2,3] (referred to Table I)

Additive	Atmosphere					
	Nitrogen			Air		
	t	L	n	t	L	n
Vitamin K_3	125	$2.5\times10^4\le M_u$	0.91	8	$10^5\le M_u$	1.0
		$M_u\le2.5\times10^4$	1.9		$2.0\times10^4\le M_u\le10^5$	0.73
	145	$3.0\times10^4\le M_u$	1.0		$M_u\le2.0\times10^4$	1.4
		$M_u\le3.0\times10^4$	2.3	21	$10^5\le M_u$	0.84
	166		0.59		$10^4\le M_u\le10^5$	0.52
	189	$10^5\le M_u$	0.59		$M_u\le10^4$	1.5
		$4.6\times10^4\le M_u\le10^5$	0.78	41	$10^4\le M_u$	0.87
		$M_u\le4.6\times10^4$	0.42		$M_u\le10^4$	3.3
	222	$9.2\times10^4\le M_u$	0.39	65	$5.6\times10^4\le M_u$	0.75
		$2.4\times10^4\le M_u\le9.2\times10^4$	0.55		$10^4\le M_u\le5.6\times10^4$	0.55
		$M_u\le2.4\times10^4$	0.40		$M_u\le10^4$	1.6
	251	$8.2\times10^4\le M_u$	0.46	95	$5.5\times10^4\le M_u$	0.76
		$1.6\times10^4\le M_u\le8.2\times10^4$	0.75		$M_u\le5.5\times10^4$	1.1
		$M_u\le1.6\times10^4$	0.32	123	$3.2\times10^4\le M_u$	0.52
					$M_u\le3.2\times10^4$	0.67

Additive	Atmosphere					
	Nitrogen			Air		
	t	L	*n*	*t*	L	*n*
				160	$3.2\times10^4\leq M_u$	0.47
					$M_u\leq3.2\times10^4$	0.69
				200	$4.0\times10^4\leq M_u$	0.43
					$M_u\leq4.0\times10^4$	0.77
Acridine	125	$2.1\times10^5\leq M_u$	0.89	8	$1.6\times10^5\leq M_u$	1.2
		$M_u\leq2.1\times10^5$	0.66		$M_u\leq1.6\times10^5$	2.4
	145	$1.3\times10^5\leq M_u$	0.90	22	$8.2\times10^4\leq M_u$	1.2
		$M_u\leq1.3\times10^5$	0.70		$M_u\leq8.2\times10^4$	2.8
	166		0.79	43	$8.0\times10^4\leq M_u$	0.91
	198	$1.5\times10^5\leq M_u$	0.75		$M_u\leq8.0\times10^4$	1.6
		$4.5\times10^4\leq M_u\leq1.5\times10^5$	0.78	74	$5.0\times10^4\leq M_u$	0.70
		$M_u\leq4.5\times10^4$	0.50		$M_u\leq5.0\times10^4$	1.6
	222	$1.2\times10^5\leq M_u$	0.56	101	$4.6\times10^4\leq M_u$	0.52
		$2.5\times10^4\leq M_u\leq1.5\times10^4$	0.74		$M_u\leq4.6\times10^4$	1.5
		$M_u\leq2.5\times10^4$	0.56	207	$2.8\times10^4\leq M_u$	0.73
	251	$6.5\times10^4\leq M_u$	0.55		$M_u\leq2.8\times10^4$	3.3
		$1.4\times10^4\leq M_u\leq6.5\times10^4$	0.97			
		$M_u\leq1.4\times10^4$	0.67			
Methylene blue				8	$8.0\times10^4\leq M_u$	1.1
					$M_u\leq8.0\times10^4$	1.5
				43	$1.1\times10^5\leq M_u$	1.2
					$M_u\leq1.1\times10^5$	1.5
				74	$1.1\times10^5\leq M_u$	1.1
					$M_u\leq1.1\times10^5$	1.4
				101	$8.0\times10^4\leq M_u$	0.70
					$M_u\leq8.0\times10^4$	2.0
				207	$7.5\times10^4\leq M_u$	0.61
					$M_u\leq7.5\times10^4$	1.5
Phenothiazine	93	$3.0\times10^5\leq M_u$	0.90	21	$2.8\times10^4\leq M_u$	0.97
		$8.0\times10^4\leq M_u\leq3.0\times10^5$	0.60		$M_u\leq2.8\times10^4$	1.7
		$M_u\leq8.0\times10^4$	0.86	41	$7.3\times10^4\leq M_u$	1.0
	115	$8.4\times10^4\leq M_u$	0.72		$M_u\leq7.3\times10^4$	1.5
		$10^4\leq M_u\leq8.4\times10^4$	0.62	65		1.0
		$M_u\leq\ 10^4$	0.86	95	$4.8\times10^4\leq M_u$	1.1
	140	$6.4\times10^4\leq M_u$	0.73		$M_u\leq4.8\times10^4$	1.9
		$M_u\leq6.4\times10^4$	0.54	123	$2.3\times10^4\leq M_u$	0.85
	175	$4.0\times10^4\leq M_u$	0.75		$M_u\leq2.3\times10^4$	2.0
		$M_u\leq4.0\times10^4$	0.56	160		1.2
	211		0.50	200	$5.1\times10^4\leq M_u$	0.72
					$M_u\leq5.1\times10^4$	1.3
p-Hydroquinone	7	$1.3\times10^5\leq M_u$	1.4	10	$1.2\times10^5\leq M_u$	1.2
		$M_u\leq1.3\times10^5$	2.3		$M_u\leq1.2\times10^5$	2.4
	20	$4.0\times10^5\leq M_u$	1.3	19	$1.2\times10^5\leq M_u$	1.3
		$6.0\times10^4\leq M_u\leq4.0\times10^5$	0.93		$M_u\leq1.2\times10^5$	2.0
		$M_u\leq6.0\times10^4$	2.3	42	$1.8\times10^5\leq M_u$	1.3
	35	$9.0\times10^4\leq M_u$	1.1		$M_u\leq1.8\times10^5$	3.9
		$M_u\leq9.0\times10^4$	1.7	65		0.89
	72	$6.0\times10^4\leq M_u$	0.52	93		1.1
		$M_u\leq6.0\times10^4$	0.91	200	$5.5\times10^4\leq M_u$	1.1
	100	$10^5\leq M_u$	0.50		$M_u\leq5.5\times10^4$	1.7
		$M_u\leq\ 10^5$	1.2			
	150	$1.2\times10^5\leq M_u$	0.47			
		$M_u\leq1.2\times10^5$	1.1			
	203	$3.3\times10^4\leq M_u$	0.58			
		$M_u\leq3.3\times10^4$	1 4			

Addtive	Atmosphere					
	Nitrogen			Air		
	t	L	n	t	L	n
Barbituric acid	7		0.75	8		1.3
	20		0.60	23		1.0
	35	$5.7\times10^4\leqq M_\mathrm{u}$	0.57	42		0.78
		$M_\mathrm{u}\leqq 5.7\times10^4$	0.84	62		0.74
	47	$5.5\times10^4\leqq M_\mathrm{u}$	0.51	91		0.53
		$M_\mathrm{u}\leqq 5.5\times10^4$	0.78	200		1.2
	72	$4.0\times10^4\leqq M_\mathrm{u}$	0.68			
		$M_\mathrm{u}\leqq 4.0\times10^4$	1.7			
	121	$4.1\times10^4\leqq M_\mathrm{u}$	0.62			
		$M_\mathrm{u}\leqq 4.1\times10^4$	1.7			
	151	$3.8\times10^4\leqq M_\mathrm{u}$	0.69			
		$M_\mathrm{u}\leqq 3.8\times10^4$	2.2			
	203	$3.5\times10^4\leqq M_\mathrm{u}$	0.77			
		$M_\mathrm{u}\leqq 3.5\times10^4$	2.8			

TABLE VIII. The Numerical Values of n for PVP Ball-Milled in the Presence of Activated Charcoal (AC) in Various Kinds of Atmosphere

$J_\mathrm{b}=0.22$, $J_\mathrm{s}=0.06$[2,3] (referred to Table I)

Kind of AC Granules Content of AC 10% Atmosphere $N_2(H_2O)$			Kind of AC Granules Content of AC 10% Atmosphere $N_2(H_2O_2)$		
t	L	n	t	L	n
118	$1.5\times10^6\leqq M_\mathrm{u}$	1.2	78	$1.8\times10^6\leqq M_\mathrm{u}$	1.3
	$M_\mathrm{u}\leqq 1.5\times10^6$	0.68		$M_\mathrm{u}\leqq 1.8\times10^6$	0.81
131	$8.4\times10^5\leqq M_\mathrm{u}$	1.2	115	$1.4\times10^6\leqq M_\mathrm{u}$	1.3
	$1.1\times10^4\leqq M_\mathrm{u}\leqq 8.4\times10^5$	0.57		$4.8\times10^4\leqq M_\mathrm{u}\leqq 1.4\times10^6$	0.75
	$M_\mathrm{u}\leqq 1.1\times10^4$	0.85		$M_\mathrm{u}\leqq 4.8\times10^4$	1.0
146	$4.5\times10^5\leqq M_\mathrm{u}$	1.2	127	$1.5\times10^6\leqq M_\mathrm{u}$	1.2
	$2.0\times10^4\leqq M_\mathrm{u}\leqq 4.5\times10^5$	0.56		$2.0\times10^4\leqq M_\mathrm{u}\leqq 1.5\times10^6$	0.57
	$M_\mathrm{u}\leqq 2.0\times10^4$	1.6		$M_\mathrm{u}\leqq 2.0\times10^4$	0.99
162	$4.5\times10^5\leqq M_\mathrm{u}$	1.2	145	$10^6\leqq M_\mathrm{u}$	1.3
	$2.0\times10^4\leqq M_\mathrm{u}\leqq 4.5\times10^5$	0.56		$2.3\times10^4\leqq M_\mathrm{u}\leqq 10^6$	0.57
	$M_\mathrm{u}\leqq 2.0\times10^4$	1.8		$M_\mathrm{u}\leqq 2.3\times10^4$	1.2
181	$2.4\times10^5\leqq M_\mathrm{u}$	0.70	164	$4.6\times10^4\leqq M_\mathrm{u}$	0.50
	$2.0\times10^4\leqq M_\mathrm{u}\leqq 2.4\times10^5$	0.51		$M_\mathrm{u}\leqq 4.6\times10^4$	1.4
	$M_\mathrm{u}\leqq 2.0\times10^4$	1.4	184	$1.1\times10^6\leqq M_\mathrm{u}$	1.2
202	$2.5\times10^5\leqq M_\mathrm{u}$	0.71		$2.5\times10^4\leqq M_\mathrm{u}\leqq 1.1\times10^6$	0.51
	$1.2\times10^4\leqq M_\mathrm{u}\leqq 2.5\times10^5$	0.44		$M_\mathrm{u}\leqq 2.5\times10^4$	1.3
	$M_\mathrm{u}\leqq 1.2\times10^4$	1.5	211	$10^6\leqq M_\mathrm{u}$	1.0
221	$10^4\leqq M_\mathrm{u}$	0.46		$3.3\times10^4\leqq M_\mathrm{u}\leqq 10^6$	0.51
	$M_\mathrm{u}\leqq 10^4$	1.6		$M_\mathrm{u}\leqq 3.3\times10^4$	1.8
			241	$3.2\times10^4\leqq M_\mathrm{u}$	0.44
				$M_\mathrm{u}\leqq 3.2\times10^4$	1.8
			269	$1.2\times10^6\leqq M_\mathrm{u}$	0.73
				$4.2\times10^4\leqq M_\mathrm{u}\leqq 1.2\times10^6$	0.49
				$M_\mathrm{u}\leqq 4.2\times10^4$	2.0

	Kind of AC Granules Content of AC 15.1% Atmosphere Air			Kind of AC Fine powders Content of AC 10% Atmosphere Air	
t	L	n	t	L	n
65		0.88	8	$1.5\times10^5\leq M_{\rm u}$	1.0
98		0.77		$M_{\rm u}\leq1.5\times10^5$	1.9
130		0.81	22	$1.4\times10^5\leq M_{\rm u}$	0.99
164		0.72		$M_{\rm u}\leq1.4\times10^5$	1.4
198	$2.1\times10^4\leq M_{\rm u}$	0.72	46	$1.4\times10^5\leq M_{\rm u}$	1.1
	$M_{\rm u}\leq2.1\times10^4$	2.3		$M_{\rm u}\leq1.4\times10^5$	1.5
251	$2.6\times10^4\leq M_{\rm u}$	0.57	63	$1.7\times10^5\leq M_{\rm u}$	0.72
	$M_{\rm u}\leq2.6\times10^4$	1.4		$M_{\rm u}\leq1.7\times10^5$	1.6
			80	$1.8\times10^5\leq M_{\rm u}$	0.64
				$M_{\rm u}\leq1.8\times10^5$	1.5
			113	$7.3\times10^4\leq M_{\rm u}$	1.1
				$M_{\rm u}\leq7.3\times10^4$	2.5
			136	$7.3\times10^4\leq M_{\rm u}$	0.90
				$M_{\rm u}\leq7.3\times10^4$	2.7

	Kind of AC Granules Content of AC 15.1% Atmosphere Oxygen			Kind of AC Granules Content of AC 10% Atmosphere $O_2(H_2O)$	
t	L	n	t	L	n
69	$7.5\times10^5\leq M_{\rm u}$	1.1	122	$1.3\times10^6\leq M_{\rm u}$	1.2
	$3.0\times10^4\leq M_{\rm u}\leq7.5\times10^5$	0.91		$1.7\times10^4\leq M_{\rm u}\leq1.3\times10^6$	0.74
	$M_{\rm u}\leq3.0\times10^4$	1.4		$M_{\rm u}\leq1.7\times10^4$	1.2
82	$3.0\times10^4\leq M_{\rm u}$	0.89	164	$1.3\times10^6\leq M_{\rm u}$	1.2
	$M_{\rm u}\leq3.0\times10^4$	1.2		$2.8\times10^4\leq M_{\rm u}\leq1.3\times10^6$	0.70
112	$3.0\times10^4\leq M_{\rm u}$	0.90		$M_{\rm u}\leq2.8\times10^4$	1.2
	$M_{\rm u}\leq3.0\times10^4$	1.4	184	$8.2\times10^5\leq M_{\rm u}$	1.4
148	$7.2\times10^5\leq M_{\rm u}$	1.0		$2.1\times10^4\leq M_{\rm u}\leq8.2\times10^5$	0.69
	$M_{\rm u}\leq7.2\times10^5$	0.80		$M_{\rm u}\leq2.1\times10^4$	1.9
164	$4.7\times10^5\leq M_{\rm u}$	1.4	202	$4.4\times10^5\leq M_{\rm u}$	1.8
	$1.3\times10^4\leq M_{\rm u}\leq4.7\times10^5$	0.73		$5.2\times10^4\leq M_{\rm u}\leq4.4\times10^5$	0.90
	$M_{\rm u}\leq1.3\times10^4$	1.4		$M_{\rm u}\leq5.2\times10^4$	2.5
204	$1.7\times10^4\leq M_{\rm u}$	0.70	221	$6.2\times10^5\leq M_{\rm u}$	1.1
	$M_{\rm u}\leq1.7\times10^4$	1.7		$2.4\times10^4\leq M_{\rm u}\leq6.2\times10^5$	0.55
224	$2.0\times10^4\leq M_{\rm u}$	0.62		$M_{\rm u}\leq2.4\times10^4$	1.8
	$M_{\rm u}\leq2.0\times10^4$	1.8	241	$6.0\times10^5\leq M_{\rm u}$	0.94
248	$8.0\times10^3\leq M_{\rm u}$	0.72		$1.4\times10^4\leq M_{\rm u}\leq6.0\times10^5$	0.48
	$M_{\rm u}\leq8.0\times10^3$	2.8		$M_{\rm u}\leq1.4\times10^4$	1.6
			271	$2.4\times10^5\leq M_{\rm u}$	0.94
				$1.4\times10^4\leq M_{\rm u}\leq2.4\times10^5$	0.52
				$M_{\rm u}\leq1.4\times10^4$	1.8

2) Relation between R and $M_{\rm u}$

A line broken at several points was obtained by the logarithmic plot of ($-\log R$) *versus* $M_{\rm u}$, as ahown in Fig. 3. The value of $M_{\rm u}$ at the broken point and the gradient of each of the straight lines in the range of various molecular weights, n, are shown in Table V, VI, VII, VIII and IX. These Tables show the existence of the critical molecular weight, $M_{\rm c}$, at the region of molecular weight above which, n is around or below 1.0, and at the region of molecular weight below which, n is larger than 1.0. The value of $M_{\rm c}$ in the absence of the additive was influenced little by the ball-milling atmosphere.

TABLE IX. Numerical Values of n for PVP Ball-Milled in the Presence of Chloranil $J_\mathrm{b}=0.43$, $J_\mathrm{s}=0.03$3) (refered to Table I)

Content of chloranil 5% Atmosphere $N_2(H_2O)$			Content of chloranil 5% Atmosphere $N_2(H_2O_2)$			Content of chloranil 5% Atmosphere Air		
t	L	n	t	L	n	t	L	n
43	$5.5\times10^5\leq M_\mathrm{u}$	1.2	55	$1.1\times10^6\leq M_\mathrm{u}$	1.6	31	$7.8\times10^5\leq M_\mathrm{u}$	0.99
	$1.6\times10^4\leq M_\mathrm{u}\leq5.5\times10^5$	0.65		$6.0\times10^4\leq M_\mathrm{u}\leq1.1\times10^6$	0.98		$1.3\times10^4\leq M_\mathrm{u}\leq7.8\times10^5$	0.73
	$M_\mathrm{u}\leq1.6\times10^4$	1.5		$M_\mathrm{u}\leq6.0\times10^4$	2.2		$M_\mathrm{u}\leq1.3\times10^4$	1.1
51	$1.3\times10^4\leq M_\mathrm{u}$	0.68	62	$4.7\times10^5\leq M_\mathrm{u}$	0.93	47	$4.7\times10^5\leq M_\mathrm{u}$	0.93
	$M_\mathrm{u}\leq1.3\times10^4$	1.4		$1.1\times10^4\leq M_\mathrm{u}\leq4.7\times10^5$	0.63		$8.6\times10^3\leq M_\mathrm{u}\leq4.7\times10^5$	0.53
55	$2.5\times10^4\leq M_\mathrm{u}$	0.70		$M_\mathrm{u}\leq1.1\times10^4$	1.2		$M_\mathrm{u}\leq8.6\times10^3$	1.2
	$M_\mathrm{u}\leq2.5\times10^4$	1.3	66	$6.0\times10^5\leq M_\mathrm{u}$	0.92	61	$6.4\times10^4\leq M_\mathrm{u}$	0.75
59	$3.8\times10^4\leq M_\mathrm{u}$	0.64		$1.6\times10^4\leq M_\mathrm{u}\leq6.0\times10^5$	0.64		$M_\mathrm{u}\leq6.4\times10^4$	0.98
	$M_\mathrm{u}\leq3.8\times10^4$	1.3		$M_\mathrm{u}\leq1.6\times10^4$	1.0	67	$8.0\times10^4\leq M_\mathrm{u}$	0.62
64	$4.5\times10^4\leq M_\mathrm{u}$	0.58	69	$2.9\times10^4\leq M_\mathrm{u}$	1.2		$M_\mathrm{u}\leq8.0\times10^4$	1.3
	$M_\mathrm{u}\leq4.5\times10^4$	1.4		$M_\mathrm{u}\leq2.9\times10^4$	1.6	73	$7.7\times10^4\leq M_\mathrm{u}$	0.35
73	$5.0\times10^4\leq M_\mathrm{u}$	0.56	75	$3.5\times10^4\leq M_\mathrm{u}$	1.1		$M_\mathrm{u}\leq7.7\times10^4$	1.4
	$M_\mathrm{u}\leq5.0\times10^4$	1.8		$M_\mathrm{u}\leq3.5\times10^4$	1.9	81	$9.5\times10^4\leq M_\mathrm{u}$	0.35
85	$5.0\times10^4\leq M_\mathrm{u}$	0.57	84	$2.8\times10^4\leq M_\mathrm{u}$	0.58		$2.5\times10^4\leq M_\mathrm{u}\leq9.5\times10^4$	1.6
	$M_\mathrm{u}\leq5.0\times10^4$	1.7		$M_\mathrm{u}\leq2.8\times10^4$	1.3		$M_\mathrm{u}\leq2.5\times10^4$	1.1
101	$5.3\times10^4\leq M_\mathrm{u}$	0.36	102	$4.1\times10^4\leq M_\mathrm{u}$	0.69	91	$5.2\times10^4\leq M_\mathrm{u}$	0.28
	$M_\mathrm{u}\leq5.3\times10^4$	1.6		$M_\mathrm{u}\leq4.1\times10^4$	1.4		$1.4\times10^4\leq M_\mathrm{u}\leq5.2\times10^4$	1.8
							$M_\mathrm{u}\leq1.4\times10^4$	1.4
						99	$4.8\times10^4\leq M_\mathrm{u}$	0.25
							$1.4\times10^4\leq M_\mathrm{u}\leq4.8\times10^4$	1.8
							$M_\mathrm{u}\leq1.4\times10^4$	1.5

Content of chloranil 10% Atmosphere Air			Content of chloranil 5% Atmosphere O_2			Content of chloranil 10% Atmosphere $O_2(H_2O)$		
t	L	n	t	L	n	t	L	n
199	$1.4\times10^6\leq M_\mathrm{u}$	1.4	36	$1.4\times10^6\leq M_\mathrm{u}$	1.3	42	$5.5\times10^4\leq M_\mathrm{u}$	1.2
	$8.4\times10^4\leq M_\mathrm{u}\leq1.4\times10^6$	0.78		$2.5\times10^4\leq M_\mathrm{u}\leq1.4\times10^6$	0.74		$1.8\times10^4\leq M_\mathrm{u}\leq5.5\times10^4$	0.75
	$M_\mathrm{u}\leq8.4\times10^4$	1.8		$M_\mathrm{u}\leq2.5\times10^4$	1.4		$M_\mathrm{u}\leq1.8\times10^4$	1.8
210	$9.0\times10^5\leq M_\mathrm{u}$	1.2	47	$1.8\times10^6\leq M_\mathrm{u}$	1.2	47	$2.8\times10^4\leq M_\mathrm{u}$	0.84
	$7.8\times10^4\leq M_\mathrm{u}\leq9.0\times10^5$	0.78		$2.8\times10^4\leq M_\mathrm{u}\leq1.8\times10^6$	0.70		$M_\mathrm{u}\leq2.8\times10^4$	1.6
	$M_\mathrm{u}\leq7.8\times10^4$	1.4		$M_\mathrm{u}\leq2.8\times10^4$	1.6	51	$6.0\times10^4\leq M_\mathrm{u}$	0.73
215	$7.4\times10^4\leq M_\mathrm{u}$	0.81	50	$10^6\leq M_\mathrm{u}$	0.73		$M_\mathrm{u}\leq6.0\times10^4$	1.3
	$M_\mathrm{u}\leq7.4\times10^4$	1.3		$3.5\times10^4\leq M_\mathrm{u}\leq10^6$	0.57	56	$8.0\times10^4\leq M_\mathrm{u}$	0.67
218	$3.8\times10^5\leq M_\mathrm{u}$	2.1		$M_\mathrm{u}\leq3.5\times10^4$	0.89		$M_\mathrm{u}\leq8.0\times10^4$	1.3
	$9.0\times10^4\leq M_\mathrm{u}\leq3.8\times10^5$	1.3	55	$2.0\times10^4\leq M_\mathrm{u}$	0.47	64	$8.7\times10^4\leq M_\mathrm{u}$	0.58
	$M_\mathrm{u}\leq9.0\times10^4$	2.2		$M_\mathrm{u}\leq2.0\times10^4$	0.63		$M_\mathrm{u}\leq8.7\times10^4$	1.4
224	$2.0\times10^5\leq M_\mathrm{u}$	1.3	61	$5.6\times10^4\leq M_\mathrm{u}$	0.52	75	$5.2\times10^4\leq M_\mathrm{u}$	0.40
	$M_\mathrm{u}\leq2.0\times10^5$	0.72		$M_\mathrm{u}\leq5.6\times10^4$	0.91		$M_\mathrm{u}\leq5.2\times10^4$	1.1
232	$1.2\times10^5\leq M_\mathrm{u}$	0.39	65	$6.0\times10^4\leq M_\mathrm{u}$	0.44	88	$5.7\times10^4\leq M_\mathrm{u}$	0.29
	$3.6\times10^4\leq M_\mathrm{u}\leq1.2\times10^5$	0.83		$M_\mathrm{u}\leq6.0\times10^4$	0.86		$M_\mathrm{u}\leq5.7\times10^4$	1.2
	$M_\mathrm{u}\leq3.6\times10^4$	1.4	72	$6.3\times10^4\leq M_\mathrm{u}$	0.39	107		2.8
241	$1.2\times10^5\leq M_\mathrm{u}$	0.50		$M_\mathrm{u}\leq6.3\times10^4$	0.84			
	$4.0\times10^4\leq M_\mathrm{u}\leq1.2\times10^5$	0.61						
	$M_\mathrm{u}\leq4.0\times10^4$	1.5						
261	$4.9\times10^4\leq M_\mathrm{u}$	0.39						
	$M_\mathrm{u}\leq4.9\times10^4$	1.4						

2)-i The Value of M_c in the Presence of Inorganic Additives

In case of ball-milling in nitrogen, n was around or below 1.0 in all the range of molecular weight in the presence of white alundum or talc. The value of M_c in the presence of sillca sands was approximately identical with the value in the absence of the additive. But in the presence of the other additives, M_c was larger than the value in the absence of the additive at the first stage after the lapse of the induction period and decreased gradually by ball-milling.

In case of ball-milling in air, n was around or below 1.0 in all the range of molecular weight in the presence of white alundum. The value of M_c in the presence of talc or the granules of activated charcoal was smaller than the value in the asbence of the additive. The value of M_c in the presence of zinc oxide was nearly identical with the value in the absence of the additive. The value of M_c in the presence of the other additives at the first stage of ball-milling was larger than the value in the absence of the additive.

2)-ii The Value of M_c in the Presence of Organic Additives

In case of ball-milling in nitrogen, M_c was approximately identical with the value in the absence of the additive at the first stage after the lapse of the induction period, but n was below 1.0 in all the range of M_u for PVP ball-milled for more than 50 hours from the time of the induction period in the presence of vitamin K_3. In the presence of acridine or phenothiazine, n was smaller than 1.0 in all the range of M_u, and the same tendency was observed at the first stage of ball-milling in the presence of barbituric acid. But, in the presence of *p*-hydroquinone, M_c was larger than the value in the absence of the additive.

In case of ball-milling in air in the presence of vitamin K_3, n was around or below 1.0 in all the range of M_u after the lapse of the induction period. In the presence of acridine or methylene blue, M_c was larger than the value in the absence of the additive at the first stage after the lapse of the induction period and decreased gradually by ball-milling. In the presence of phenothiazine, M_c was nearly identical with the value in the absence of the additive, and in the presence of *p*-hydroquinone, M_c was larger than the value in the absence of the additive. A straight line was obtained by the logarithmic plot of $-\log R$ *versus* M_u in the presence of barbituric acid, and n was larger than 1.0 at the first stage of ball-milling.

2)-iii Influence of the Ball-Milling Atmosphere on M_c

In case of ball-milling in various kinds of atmosphere in the presence of the granules of activated charcoal, n was around or below 1.0 in all the range of M_u at the first stage, and M_c was smaller than or nearly identical with the value in the absence of the additive for PVP ball-milled for more than 20 hours from the time of the induction period. In the presence of the fine powders of activated charcoal in air, M_c was larger than the value in the absence of the additive.(Table VIII)

In the presence of chloranil in various kinds of atmosphere, M_c was nearly identical or smaller than the value in the absence of the additive at the first stage of ball-milling from the time of the induction period (Table IX).

Equation (8) is obtained by differentiating equation (4) with ball-milling time, t.

$$-\partial R/\partial M_u = nkM_u^{(n-1)}R \tag{8}$$

In equation (8), $-\partial R/\partial M_u$ is the ratio of the weight of the polymers of molecular weight between M_u and $M_u+\partial M_u$ to the total weight of the polymers. When n is larger than 1.0, $-1/R(\partial R/\partial M_u)$ decreases with a decrease of M_u. Accordingly, it is considered that the weight of the polymers in each fraction decreases with a decrease of molecular weight in the range of M_u below M_c.

Baramboim investigated a decrease of molecular weight of several kinds of polymers by the mechanical treatment and found that the molecular weight approached to the limited value between 4×10^3 and 1.1×10^4.8) It was reported in the previous paper that the molecular weight of PVP varied from 9.7×10^5 to a lower value and approached to 4×10^3 by ball-milling.7) But an appreciable decrease of molecular weight was not observed by ball-milling PVP of 7.5×10^3 of mean molecular weight, even after ball-milling for 200 hours.9) In many cases in the absence and in the presence of various kinds of the additives, the molecular weight distribution of PVP approached to the narrow distribution with the peak of a fixed low molecular weight by ball-milling, as reported in the previous papers2,7,9) and as shown in Fig. 1 and 2. Blundel, *et al.* also found the similar phenomenon by investigating molecular weight distribution of the polyethylene crystals degraded by nitric acid etching, and considered that there was a surprising regularity in the break-down pattern, indicative of certain discrete length which must be related to the way the chains were arranged in the crystals.10) These findings are considered to be related to the existence of M_c.

3) Variation of R with the Ball-Milling Time

The values of$(-\log R)$ for 10^6, 5×10^5, 10^5, 5×10^4 and 10^4 of M_u were obtained by reading the values on the log $(-\log R)$-log M_u line. As shown in Fig. 7, equation (9) was applied to the variation of R with the ball-milling time, t, where k_t, k_t', γ_1 and γ_2 were parameters dependent on the ball-milling condition and so on, and t_c was the time at which the line obtained by the logarithmic plot of $(-\log R)$ *versus* $(t-t_{ie})$ broke.

$$\begin{aligned} t<t_c \quad & R=\exp\{-k_t(t-t_{ie})^{\gamma_1}\} \\ t\geq t_c \quad & R=\exp\{-k_t'(t-t_{ie})^{\gamma_2}\} \end{aligned} \tag{9}$$

Table X, XI, XII, XIII and XIV show the numerical values of the parameters t_c, γ_1 and γ_2. When a straight line was obtained by the logarithmic plot of $(-\log R)$ versus $(t-t_{ie})$, the gradient of the line was considered to be γ_2 (Fig. 8).

In case of ball-milling in nitrogen in the presence of white alundum or barbituric acid, γ_2 decreased with a decrease of M_u. In the presence of sodium chloride in nirtogen or in the presence of the granules of activated charcoal in air, γ_2 was independent of M_u. But, in the other cases, γ_2 increased with a decrease of M_u in the range of M_u above 5×10^4.

Equation (10) was obtained by differentiating equation (9) with ball-milling time, t.

$$-\partial R/\partial t=\gamma_2\cdot k_t'(t-t_{ie})^{(\gamma_2-1)}R \tag{10}$$

In equation (10), $-\partial R/\partial t$ is the ratio of the weight of the polymers whose molecular weight varies from the value above M_u to the value below M_u by the mechanical treatment for the

TABLE X. Numerical Values of γ_1, γ_2 and t_c for Ball-Milling PVP in the Absence of the Additive
$J_b=0.22$, $J_s=0.06$7) (referred to Table I)

M_u	Atmosphere								
	Nitrogen			Air			Oxygen		
	t_c(hr)	γ_1	γ_2	t_c(hr)	γ_1	γ_2	t_c(hr)[a]	γ_1	γ_2
10^6	56	0	0.47			0.24	53	—	0.50
5×10^5	43	0.04	0.46			0.28	53	—	0.53
10^5	42	0.25	0.77	51	0.37	0.52	53	—	0.74
5×10^4	55	0.40	0.90	53	0.38	0.63	53	—	0.86
10^4							53	—	0.37

a) The value of γ_1 in case of ball-milling in oxygen could not be obtained, as the data were not sufficient for the calculation. But the same tendency as observed in nitrogen or air was also obtained for γ_1 in oxygen.

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8) N.K. Baramboim, *Dokl. Akad. Nauk SSSR*, **114**, 568 (1957); *Zhur. Fiz. Khim.*, **32**, 433 (1958).
9) N. Kaneniwa and A. Ikekawa, *Yakuzaigaku*, **31**, 201 (1971).
10) D.J. Blundell, A. Keller, and I.M. Ward, *Polymer Letters*, **4**, 781 (1966).

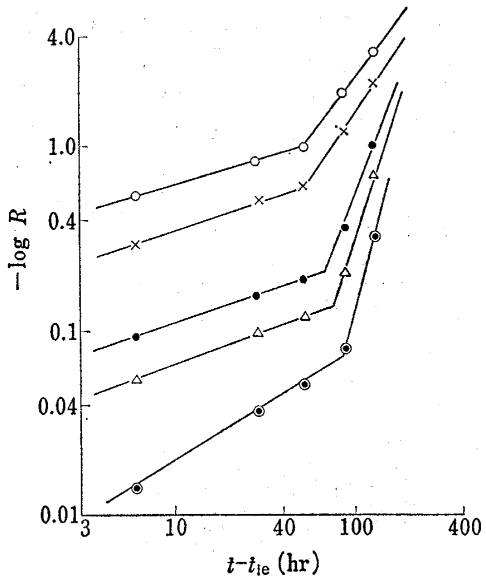

Fig. 7. Relation between R and Ball-Milling Time for Ball-Milling PVP in Nitrogen in the Presence of 10% of Phenotiazine

t_{ie}=87 (hr), $J_b=0.22$, $J_s=0.06$[3] (referred to Table I).
M_u: ○, 10^6; ×, 5×10^5; ●, 10^5; △, 5×10^4; ⊙, 10^4.

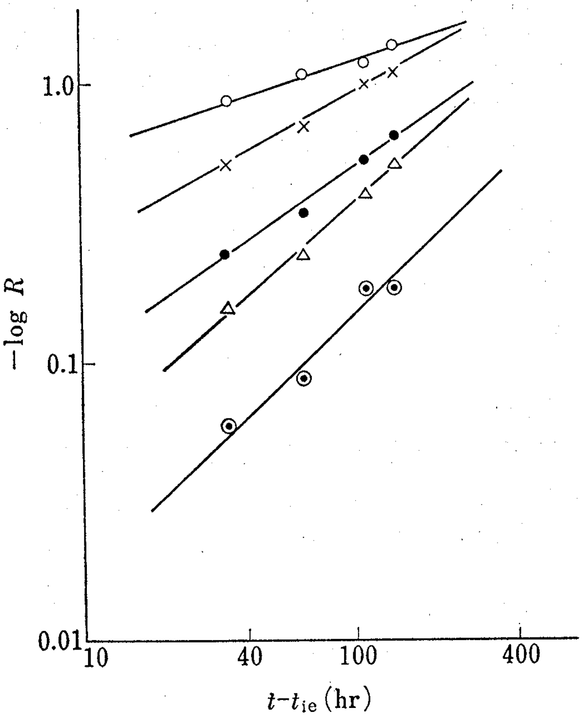

Fig. 8. Relation between R and Ball-Milling Time for Ball-Milling PVP in Air in the Presence of 10% v/v of Talc

t_{ie}=66 (hr), $J_b=0.22$, $J_s=0.06$[3] (referred to Table I).
M_u: ○, 10^6; ×, 5×10^5; ● 10^5; △, 5×10^4; ⊙, 10^4.

TABLE XI. The Numerical Values of γ_1,γ_2 and t_c for Ball-Milling PVP in the Presence of Inorganic Powders

$J_b=0.22$, $J_s=0.06$[2,3] (referred to Table I)

Additive	White alundum						Silica sands		Zinc oxide			
Atmosphere	Nitrogen			Air			Nitrogen	Air	Nitrogen			Air
M_u	t_c(hr)	γ_1	γ_2	t_c(hr)	γ_1	γ_2	γ_2	γ_2	t_c(hr)	γ_1	γ_2	γ_2
10^6	21	0.36	1.0	30	0.37	0.81	0.46	0.53	108	0.20	0.98	0.43
5×10^5	24	0.38	1.1	30	0.49	0.90	0.59	0.74	126	0.50	1.1	0.53
10^5	26	0.51	0.99	48	0.72	1.3	0.86	1.1			1.2	0.84
5×10^4			0.73	42	0.62	1.5	0.97	1.1			1.6	0.90
10^4			0.75	41	0.51	2.1	1.6				1.5	

Additive	Barium sulfate	Sodium chloride				Talc	
Atmosphere	Air	Nitrogen			Air	Nitrogen	Air
M_u	γ_2	t_c(hr)	γ_1	γ_2	γ_2	γ_2	γ_2
10^6	0.66	145	0.29	2.3	0.77	0.85	0.30
5×10^5	0.76	125	0.35	1.7	0.99	1.0	0.57
10^5	0.98	115	0.55	1.9	1.5	1.4	0.70
5×10^4	1.8	95	0.53	1.7	1.6	1.5	0.88
10^4	2.0			2.7	0.18	1.5	0.90

TABLE XII. The Numerical Values of γ_1, γ_2 and t_c for Ball-Milling PVP in the Presence of 10% of Organic Powders

$J_b=0.22$, $J_s=0.06$[2,3] (refered to Table I)

Additive	Vitamin K_3				Acridine				Methylene blue	Phenothiazine					
Atmosphere	Nitrogen			Air	Nitrogen			Air	Air	Nitrogen			Air		
M_u	t_c(hr)	γ_1	γ_2	γ_2	t_c(hr)	γ_1	γ_2	γ_2	γ_2	t_c(hr)	γ_1	γ_2	t_c(hr)	γ_1	γ_2
10^6	150	0	0.83	0.42	152	0.12	0.78	0.73	1.1	140	0.29	1.3	155	—	0.35
5×10^5	150	0	1.1	0.47	157	0.09	1.2	0.84	1.2	140	0.34	1.5	155	—	0.87
10^5			1.3	0.66	154	0	1.6	1.4	1.2	160	0.33	2.9	155	—	1.3
5×10^4			1.3	0.66	157	0	1.7	1.7	1.3	160	0.36	3.0	155	—	1.4
10^4			1.2	0.66	146	0.14	1.6	2.4		170	0.65	3.5			0.76

Additive	p-Hydroquinone						Barbituric acid					
Atmosphere	Nitrogen			Air			Nitrogen			Air		
M_u	t_c(hr)	γ_1	γ_2	t_c(hr)	γ_1	γ_2	t_c(hr)	γ_1	γ_2	t_c(hr)	γ_1	γ_2
10^6			0.49	34	0.21	1.7	46	0.32	1.6			0.62
5×10^5	40	0.52	1.5	32	0.19	1.8	48	0.37	1.6			0.81
10^5			1.5	20	0.09	1.8	46	0.58	1.3	68	1.3	2.3
5×10^4			1.8	18	0.55	2.0	54	0.72	1.2	90	1.1	2.6
10^4			2.8			0.50			0.23			

TABLE XIII. The Numerical Values of γ_1, γ_2 and t_c for Ball-Milling PVP in the Presence of Activated Charcoal (AC) in Various Kinds of Atmosphere

$J_b=0.22$, $J_s=0.06$[2,3] (referred to Table I)

Kind of AC	Granules			Granules	Granules	Fine powders	Granules	Granules
Content of AC	10%			10%	15.1%	10%	15.1%	10%
Atmosphere	$N_2(H_2O)$			$N_2(H_2O_2)$	Air	Air	O_2	$O_2(H_2O)$
M_u	t_c(hr)	γ_1	γ_2	γ_2	γ_2	γ_2	γ_2	γ_2
10^6			0.53	0.36	1.0	0.70	0.37	0.98
5×10^5	162	0.55	1.1	0.43	1.0	0.96	0.68	0.97
10^5	166	0.51	1.4	0.48	1.1	1.5	1.1	1.3
5×10^4	166	0.54	1.8	0.51	1.0	1.1	1.1	1.3
10^4	163	0.21	2.6	0	1.5		0.96	1.5

TABLE XIV. The Numerical Values of γ_1, γ_2 and t_c for Ball-Milling PVP in the Presence of Chloranil in Various Kinds of Atmosphere

$J_b=0.43$, $J_s=0.03$[3] (referred to Table I)

Content of chloranil	5%	5%	5%	10%			5%	5%		
Atmosphere	$N_2(H_2O)$	$N_2(H_2O_2)$	Air	Air			O_2	$O_2(H_2O)$		
M_u	γ_2	γ_2	γ_2	t_c(hr)	γ_1	γ_2	γ_2	t_c(hr)	γ_1	γ_2
10^6	0.68	—	0.32				0.66	54	0.40	0.55
5×10^5	0.67	—	0.56		1.5		0.69	56	0.43	0.79
10^5	0.98	1.0	1.0	227	1.4	0.68	0.91	59	0.57	1.1
5×10^4	0.98	1.1	1.5	224	2.2	0.86	0.99	62	0.42	2.4
10^4	0.47	0.61	0.80			0.39	0.99	64	0.39	—

time, ∂t, to the total weight of the polymers. The value of $-(1/R)(\partial R/\partial t)$ increases with the lapse of the ball-milling time when γ_2 is larger than 1.0, and decreases when γ_2 is smaller than 1.0. Equation (10) seems to suggest that the mean density of the activated bonds on a polymer molecule ,γ, increases with a decrease of molecular weight of PVP, when γ_2 increases with a decrease of M_u, and that the opposite is the case when γ_2 decreases with a decrease of M_u.

TABLE XV. The Numerical Values of M_c, and n_o, $R_{\gamma 1}$ and $R_{\gamma 2}$ for Ball-Milling PVP in the Presence of Inorganic or Organic Powders

$J_b=0.22$, $J_s=0.06^{2,3,7)}$ (referred to Table I)

Additive	Atmosphere	M_c	n_o	$R_{\gamma 1}$	$R_{\gamma 2}$
Absent	Nitrogen	$(4-6)\times10^4$	0.9		1.9
Absent	Air	$(3-5)\times10^4$	0.7		2.6
Absent	Oxygen	$(3-4)\times10^4$	0.7		1.7
White alundum	Nitrogen		0.7—0.8		0.72
White alundum	Air		1.0	1.7	1.8
Silica sands	Nitrogen	$(2-4)\times10^4$	0.9		2.1
Silica sands	Air	3.5×10^5	1.0—1.2		1.4
Zinc oxide	Nitrogen	$(5-6)\times10^4$	1.1—1.2		1.6
Zinc oxide	Air	$(4-6)\times10^4$	1.0		2.1
Barium sulfate	Air	7×10^4	0.9—1.1		2.8
Sodium chloride	Nitrogen	2×10^5	0.9—1.0	1.8	0.74
Sodium chloride	Air	$(7-8)\times10^4$	1.0		2.1
Talc	Nitrogen		1.0—1.2		1.7
Talc	Air		0.9		2.9
Vitamin K_3	Nitrogen	$(2.5-3)\times10^4$	0.9—1.0		2.2
Vitamin K_3	Air		0.7—1.0		1.6
Acridine	Nitrogen		0.6—1.0		2.2
Acridine	Air	8×10^4	1.0		2.3
Methylene blue	Air	10^5	1.1		1.2
Phenothiazine	Nitrogen		0.6—1.0	1.2	2.3
Phenothiazine	Air	$(2-5)\times10^4$	0.9—1.0		4.0
p-Hydroquinone	Nitrogen	$(1-2)\times10^5$	1.0—1.4		1.2
p-Hydroquinone	Air	$(1-2)\times10^5$	1.2—1.3		1.2
Barbituric acid	Nitrogen		0.8	2.3	0.76
Barbituric acid	Air		1.2—1.3		4.3

TABLE XVI. The Numerical Values of M_c, n_o, $R_{\gamma 1}$ and $R_{\gamma 2}$ for Ball-Milling PVP in the Presence of Activated Charcoal (AC) or Chloranil

Additive	Content of additive (%)	Atmosphere	M_c	n_o	$R_{\gamma 1}$	$R_{\gamma 2}$
AC (Granules)	10	$N_2(H_2O)$	$(1-2)\times10^4$	0.7	1.0[a]	3.4
AC (Granules)	10	$N_2(H_2O_2)$		0.6—1.1[b]		1.4
AC (Granules)	15.1	Air		0.8		1.0
AC (Fine powders)	10	Air	1.4×10^5	1.0		1.5
AC (Granules)	15.1	O_2	$(1-2)\times10^4$	0.8—1.0		3.2
AC (Granules)	10	$O_2(H_2O)$	$(2-3)\times10^4$	0.7—0.9		1.3
Chloranil	5	$N_2(H_2O)$	$(1-2.5)\times10^4$	0.7		1.4
Chloranil	5	$N_2(H_2O_2)$	10^4	0.6—1.0		—
Chloranil	5	Air		0.9—1.0		4.7
Chloranil	10	Air	$(7-8)\times10^4$	0.8	1.5[a]	
Chloranil	5	O_2	$(2-3.5)\times10^4$	0.8		1.5
Chloranil	5	$O_2(H_2O)$	$(3-9)\times10^4$	0.9	1.1	4.3

[a] In these cases, the ratio of γ_1 for PVP of M_u of 5×10^4 to γ_1 for PVP of M_u of 5×10^5 was shown for the data of γ_1 for PVP of M_u of 10^6 could not be obtained.

[b] The value of n_o was approximately 0.6 for PVP of molecular weight, M_u, above 2×10^4 and 1.1 for PVP of M_u below 2×10^4.

AC, $J_b=0.22$, $J_s=0.06^{2,3)}$; Chloranil, $J_b=0.43$, $J_s=0.03^{3)}$ (referred to Table I).

4) Discussion on the Way How the Chains are broken

Though equation (5) is very complicated, it is suggested from this equation that, in case of the random chain scission, the parameter n in equation (4) is larger than 1.0, when $\gamma(M_i)$ increases with an increase of M_i, and that n is smaller than 1.0 in the opposite case. The parameter n varied with the ball-milling time, as shown in Table V, VI, VII, VIII and IX. The value of n in the range of M_u above M_c after ball-milling for an infinitely short time from the time of the induction period, n_0, was obtained by extrapolating the $\log n - (t - t_{ie})$ curve. Table XV and XVI show the numerical values of n_0 and the ratio of the value of γ_1 or γ_2 for PVP of M_u of 5×10^4 to the value for PVP of M_u of 10^6, R_{γ_1} or R_{γ_2}, respectively. The following suggestion seems to be reasonable from the comparison of n_0 and R_{γ_1} or R_{γ_2}.

In case of ball-milling in air in the presence of barbituric acid, n_0 was little larger than 1.0 and R_{γ_2} was larger than 1.0. In this case, the probability of chain scission at the center of a polymer may be a little higher than the probability near the end of a polymer. But, in the other cases, n_0 was around or below 1.0, and R_{γ_1} and R_{γ_2} were approximately equal to or larger than 1.0. In case of ball-milling in nitrogen in the presence of white alundum, n_0 was smaller than 1.0, and γ_1 increased with a decrease of M_u, as shown in Table XI. In these cases, random chain scission is most probable and the value of γ for PVP of low molecular weight seems to be approximately equal to or larger than the value for PVP of high molecular weight.

Roughly speaking, the following tendency was observed. The peak in the molecular weight distribution curve of PVP shifted from approximately 10^6 to lower molecular weight by ball-milling and the value of β_e was large, when R_{γ_2} was around or below 1.0 or when the probability of chain scission at the center seemed to be a little larger than the probability near the end of a polymer.

Experimental

The ball-milled samples reported in the previous papers were used.[2,3,7] The molecular weight distribution of PVP in the supernatant obtained by centrifugal separation of $KH_2PO_4 \cdot Na_2HPO_4$ buffer solution (pH: 6.3, ionic strength; 0.05) of the ball-milled sample was investigated by gel permeation method and by viscometry reported in the previous papers.[2,7]