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Influence of Addition of Organic and Inorganic Powders on Degradation of Polyvinylpyrrolidone by Ball-Milling in Air

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Degradation of polyvinylpyrrolidone (PVP) by ball-milling in air in the presence of each of the seven kinds of organic powders and seven kinds of inorganic powders with Mohrse's hardness between 1 and 9 was investigated. The organic powders added to PVP were chloranil and Vitamin K_3 (good electron accepters), phenothiazine (a good electron donor), acridine and methylene blue (good electron accepters and good electron donors at the same time), and *p*-hydroquinone and barbituric acid (poor electron donors and poor electron accepters as well).

The rate of a decrease of molecular weight of PVP by ball-milling was represented by equation (1).

$$\begin{aligned} t < t_i \quad & -dM/dt = 0 \\ t \geq t_i \quad & -dM/dt = k_m \cdot M^{\beta} \end{aligned} \qquad (1)$$

In case of the addition of organic powders, β was larger than 1.0 in the presence of poor electron donors, and approximately equal to 1.0 in the presence of good electron donors. In case of the addition of inorganic powders, β was between 0.4 and 1.9. In the presence of hard powders, t_i was zero and β was large. In the presence of soft powders, β was small and t_i was larger than zero.

In case of the addition of *p*-hydroquinone, barbituric acid or hard inorganic powders other than silica sands and zinc oxide, the peak in the molecular weight distribution curve of PVP shifted from the molecular weight of approximately 10^6 to lower molecular weight with the lapse of ball-milling time. In case of the addition of the other powders, the original peak decreased and a new peak at molecular weight lower than that of the original peak increased by ball-milling.

It was reported in the previous paper that degradation of polyvinylpyrrolidone (PVP) by ball-milling was influenced by the atmosphere.[2] In this paper, degradation of PVP by ball-milling in air in the presence of organic and inorganic powders was studied, and how the rate of a decrease of molecular weight of PVP by ball-milling was influenced by the ability of an organic additive to donate or to accept an electron and by Mohrse's hardness of an inorganic additive was investigated.

Experimental

The materials used were PVP K90 purchased from Wako Junyaku Kogyo Co., PVP K15 purchased from Tokyo Kasei Kogyo Co., seven kinds of organic powders tabullated in Table I and seven kinds of inorganic powders tabullated in Table II. The energy of an electron in an orbital, E, is expressed by equation (1), where α is a Coulomb integral and β is a resonance integral.[3]

$$E = \alpha + k\beta \qquad (1)$$

In Table I are shown the numerical values of k for the highest occupied orbital and the lowest unoccupied orbital of each of the organic additives.[3] In Table II, true density of the granules of activated charcoal was measured in distilled water and those of the other materials were measured with a Toshiba-Beckmann air comparison picnometer. Mohrse's hardness[4] of white alundum was assumed to be equal to that of alundum.

1) Location: *Hatanodai, 1-5-8, Shinagawa-ku, Tokyo.*
2) N. Kaneniwa and A. Ikekawa, *Chem. Pharm. Bull.* (Tokyo), **20**, 1536 (1972); *idem*, *Zairyo*, **21**, 516 (1972).
3) K. Hirano, "Bunshi Seibutsugaku Nyumon," Hirokawa Shoten, 1966, p. 31.
4) Nihon Kagaku-kai, "Kagaku Benran," Kisohen II, Maruzen, 1966, p. 475.

Table I. The Value of k for Organic Additives

Additives	k for the highest occupied orbital	k for the lowest unoccupied orbital
Chloranil	0.753	−0.275
Vitamin K_3	0.915	−0.340
Acridine	0.494	−0.342
Methylene blue	0.398	−0.354
Phenothiazine	−0.210	−1.000
p-Hydroquinone	1.000	−1.175
Barbituric acid	1.033	−1.295

Table II. Physical Properties of Inorganic Additives

Additives	True density	Mohrse's hardness
White alundum (type 40)	3.90	9
Silica sands (type 3)	2.65	7
Zinc oxide	5.63	4—4.5
Barium sulfate	4.99	2.5—3.5
Sodium chloride	2.16	2—2.5
Activated charcoal	2.15	1—2
Talc	3.04	1

The granules of activated charcoal were cylindrical in diameter of 3 mm and in length between 5 mm and 8 mm. The particles of talc were blocky with a weight mean diameter of approximately 8.3 mm. Zinc oxide and barium sulfate were fine powders.

To 18 grams of PVP K90 was added 2 grams of each of the organic additives or each of the inorganic additives whose true volume was one tenth of that of the mixture. The mixture was ball-milled in the way reported in the previous paper.[2] Viscosity mean molecular weight and molecular weight distribution of PVP in the supernatant obtained by centrifugal separation of KH_2PO_4–Na_2HPO_4 buffer solution (pH: 6.30, ionic strength: 0.05) of approximately 50 mg of the ball-milled sample were investigated according to the methods reported in the previous paper.[2] When an organic additive was mixed in the test solution of PVP, the concentration of PVP in the solution obtained by the measurement of the absorbance at 215 nm was corrected by the measurement of the absorbance at the absorption maximum for the additive. Permeability of ball-milled PVP through cellulose membrane was investigated as follows; Approximately 100 mg of the sample was dissolved in 5 ml of distilled water. Cellulose tubing purchased from Sanko Junyaku Co. and containing the solution was immersed in 40 ml of distilled water for seventeen hours. Then, the ratio of the amount of PVP in the cellulose tubing to that out of the tubing was obtained by the measurement of the absorption intensity at 215 nm. UV spectra of the solutions of ball-milled samples were measured with a Hitachi recording Spectrophotometer (Type EPS-3). IR spectra of ball-milled samples were measured with a JASCO granting infrared spectrophotometer (Type IRA-1).

Result and Discussion

Fig. 1 shows the influence of the addition of organic powders on a decrease of molecular weight of PVP by ball-milling. The rate of a decrease of molecular weight of PVP decreased when one of the absolute value of k for the additive in Table I was relatively small. Molecular weight of PVP did not decrease by ball-milling for 200 hours in the presence of chloranil which was a good electron accepter. The rate was influenced little by the addition of the powders whose absolute values of k were both relatively small. On the contrary, the rate increased by the addition of the powders whose absolute values of k were both large.

Fig. 2 shows the influence of the addition of inorganic powders on a decrease of molecular weight of PVP by ball-milling. The rate of a decrease of molecular weight of PVP increased at the first stage of ball-milling in case of the addition of hard powders, such as white alundum and silica sands. In case of the addition of soft powders, such as activated charcoal and talc,

an induction period was observed, after the lapse of which molecular weight of PVP began to decrease.

Fig. 3, 4, 5 and 6 show the change in molecular weight distribution of PVP by ball-milling in the presence of one of the organic powders in Table I. In case of the addition of barbituric acid or *p*-hydroquinone, the peak in the molecular weight distribution curve of PVP shifted from the molecular weight of approximately 10^6 to lower molecular weight with the lapse

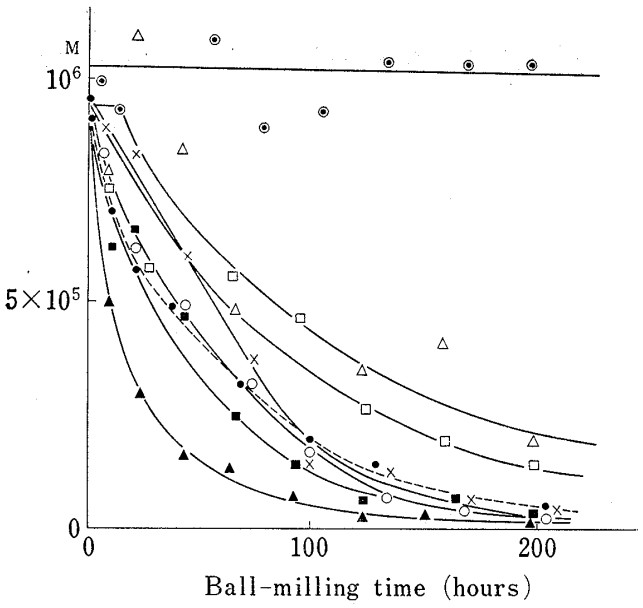

Fig. 1. Influence of Addition of Organic Powders on Decrease of Molecular Weight of PVP by Ball-Milling

organic powders
absent: ------●------ methylene blue: —×—
chloranil: —⊙— phenothiazine: —△—
vitamin K_3: —□— *p*-hydroquinone: —■—
acridine: —○— barbituric acid: —▲—

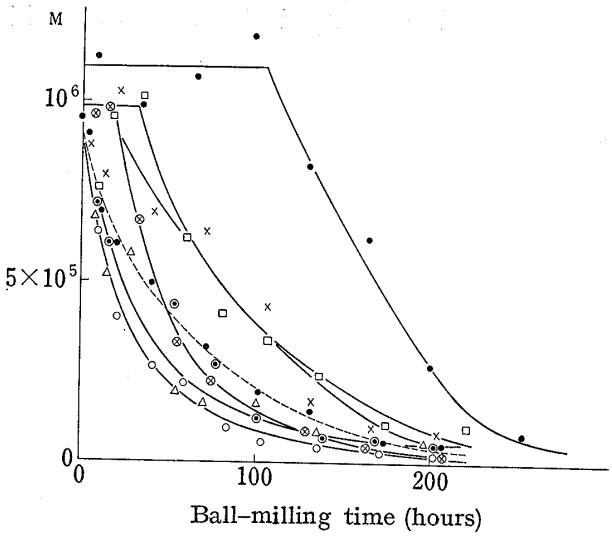

Fig. 2. Influence of Addition of Inorganic Powders on Decrease of Molecular Weight of PVP by Ball-Milling

inorganic powders
---●---: absent; —○—: white alundum; —△—: silica sand; —□—: zinc oxide; —⊙—: barium sulfate; —⊗—: sodium chloride; —●—: activated charcoal, granular; —×—: talc

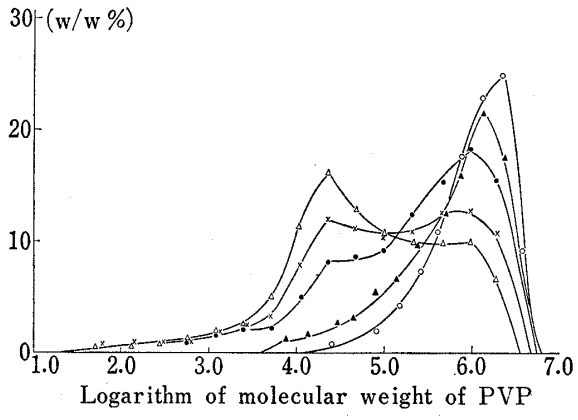

Fig. 3. Change in Molecular Weight Distribution of PVP by Ball-Milling with Vitamin K_3

ball-milling time (hr)
0: ○; 95: ▲; 123: ●; 160: ×; 200: △;

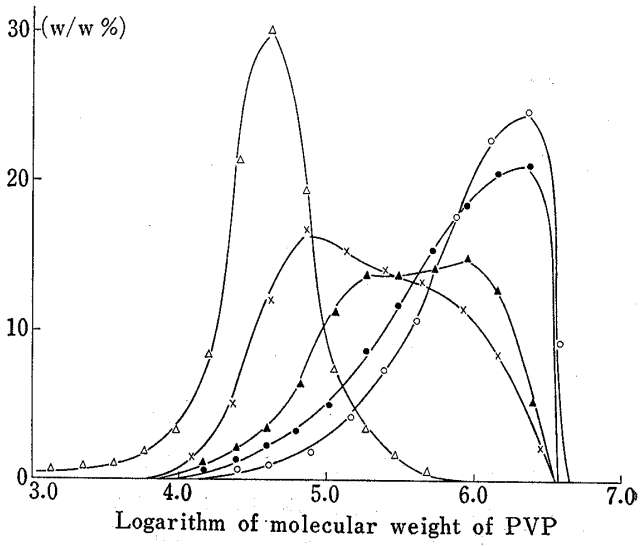

Fig. 4. Change in Molecular Weight Distribution of PVP by Ball-Milling with Methylene Blue

ball-milling time (hr)
0: ○; 22: ●; 74: ▲; 101: ×; 207: △

of ball-milling time. In case of the addition of the other powders, the peak at the molecular weight of approximately 10^6 decreased and a new peak appeared at lower molecular weight. The new peak increased, shifting to lower molecular weight with the lapse of ball-milling time, in the presence of acridine or methylene blue. In the presence of Vitamin K_3, the new peak increased but shifted slightly by ball-milling.

Fig. 7, 8, 9 and 10 show the influence of the addition of inorganic powders on the change in molecular weight distribution of PVP by ball-milling. The change in the presence of white alundum was similar to the change in the presence of *p*-hydroquinone or barbituric acid. The same tendency was also obtained in case of the addition of barium sulfate and sodium chloride. The change in the presence of silica sands was similar to the change in the presence

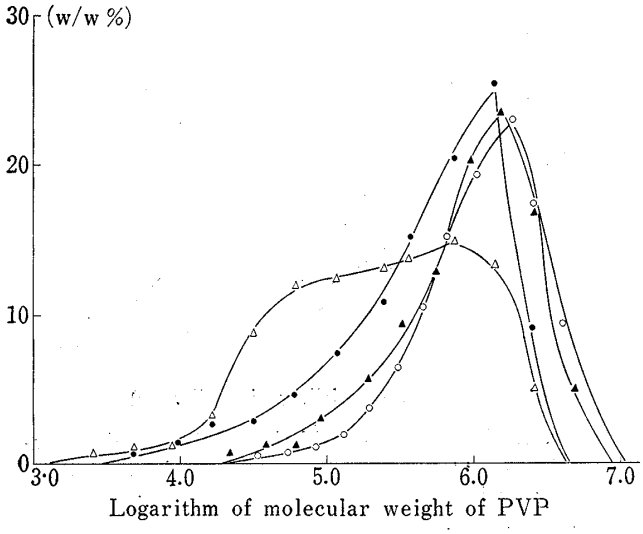

Fig. 5. Change in Molecular Weight Distribution of PVP by Ball-Milling with Phenothiazine

ball-milling time (hr)
0: ○; 95: ▲; 123: ●; 200: △

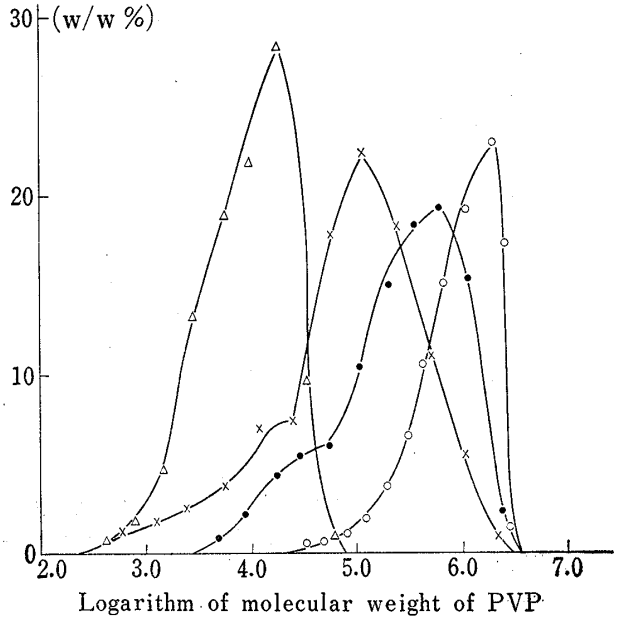

Fig. 6. Change in Molecular Weight Distribution of PVP by Ball-Milling with Barbituric Acid

ball-milling time (hr)
0: ○; 23: ●; 62: ×; 200: △;

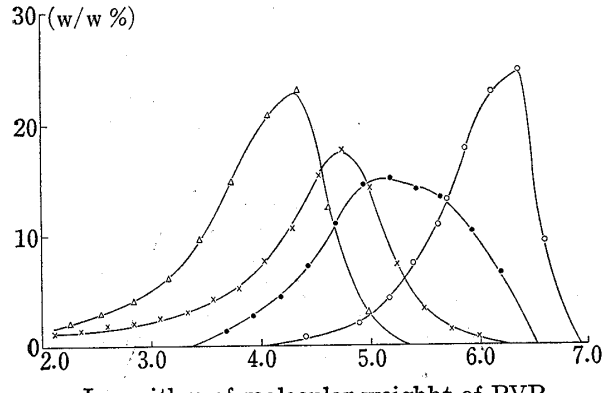

Fig. 7. Molecular Weight Distribution of PVP Containing 10 v/v % of White Alundum changed by Ball-Milling

ball-milling time (hr)
0: ○; 30: ●; 103: ×; 200: △;

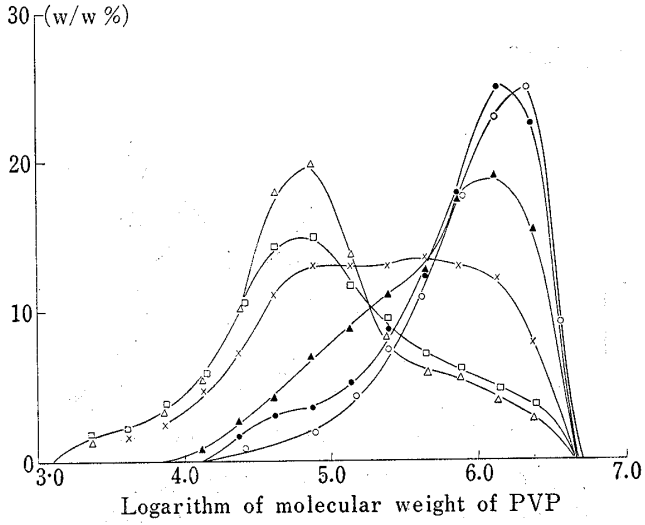

Fig. 8. Change in Molecular Weight Distribution of PVP by Ball-Milling with Zinc Oxide

ball-milling time (hr)
0: ○; 59: ●; 80: ▲; 106: ×; 172: □; 200: △;

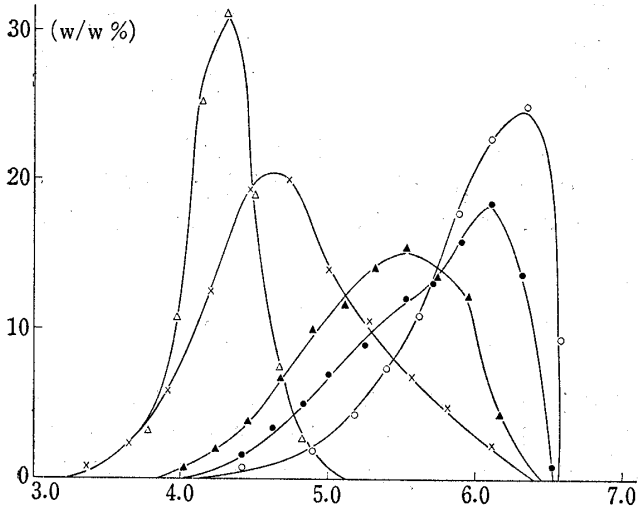

Fig. 9. Change in Molecular Weight Distribution of PVP by Ball-Milling with Sodium Chloride

ball-milling time (hr)
0: ○; 30: ●; 55: ▲; 100: ×; 200: △

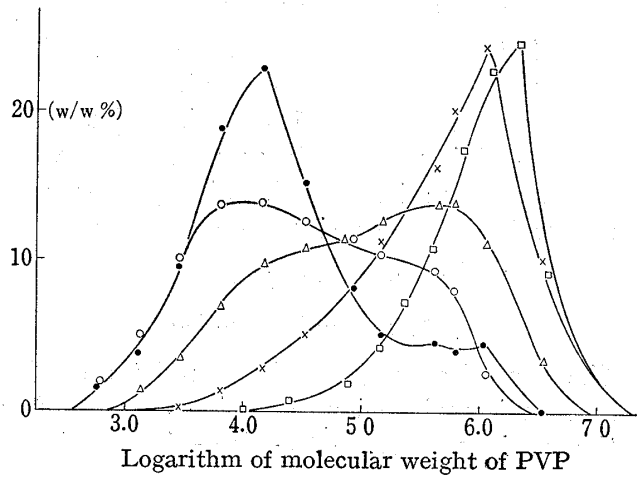

Fig. 10. Change in Molecular Weight Distribution of PVP Containing 10v/v % of Talc by Ball-Milling

ball milling time (hr)
0: □; 60: ×; 100: △; 130: ○; 200: ●

of acridine or methylene blue. The change in the presence of zinc oxide, activated charcoal or talc was similar to the change in the presence of Vitamin K_3.

Baramboim reported that the lowest molecular weight obtained by ball-milling several kinds of synthetic polymers for infinitely long time, M_∞, was between 6×10^3 and 2×10^4.[5] In the previous paper, it was reported that M_∞ for ball-millig of PVP was approximately 4×10^3.[2] In our another paper, it was shown that apparent increase or decrease of molecular weight was not observed by ball-milling PVP K15 with mean molecular weight of 7.5×10^3 in nitrogen for 150 hours or in oxygen for 200 hours.[6] But as shown in Fig. 3, 4, 5, 6, 7, 8, 9 and 10, much amount of PVP with molecular weight lower than 4×10^3 was produced in case of the addition of organic or inorganic powders. Table III shows permeability of ball-milled PVP through cellulose membrane. It was considered from the above findings that molecular weight of PVP which permeated through the membrane was lower than 10^3. It may be more difficult to cut off main chains of PVP with molecular weight below 4×10^3 than to cut off those with molecular weight above 4×10^3. Mechanism of cutting off of a

Table III. Permeability of Ball-Milled PVP through Cellulose Membrane

Additive	Atmosphere	Ball-milling time (hr)	P (w/w%)[a]
Absent	nitrogen	420[5]	6.7
Absent	air	420[5]	6.1
Absent	oxygen	420[5]	9.6
White alundum	air	200	3.5
Silica sands	air	200	0.5
Zinc oxide	air	200	7.8
Barium sulfate	air	200	2.5
Sodium chloride	air	200	4.1
Activated charcoal	air	250	1.3
Talc	air	200	0.9

a) Percentage by weight of PVP which permeated through cellulose membrane.

5) N.K. Baramboim, *Doklady Akad. Nauk SSSR*, **114**, 568 (1957); *idem*, *Zhur. Fiz. Khim.*, 32, 433 (1958).
6) N. Kaneniwa and A. Ikekawa, *Yakuzaigaku*, **31**, 201 (1971); *idem*, *Zairyo*, **20**, 720 (1971).

main chain of a PVP molecule with molecular weight below 4×10^3 may be different from that with molecular weight above 4×10^3. In any case, it is considered from the above findings that the molecular weight of PVP obtained by ball-milling for infinitely long time is as low as that of a monomer unit.

As shown in Fig. 11, equation (2) applied well to a decrease of molecular weight of PVP by ball-milling, where M was molecular weight of the sample after ball-milling for t hours, t_i was an induction period, and k_m and β were parameters dependent on physical and chemical properties of an additive and so on.

$$\begin{aligned} t < t_i \quad & -dM/dt = 0 \\ t \geq t_i \quad & -dM/dt = k_m \cdot M^{\beta} \end{aligned} \tag{2}$$

The numerical values of k_m, β and t_i are tabullated in Table IV. The values for the case of ball-milling without an additive were obtained by application of equation (2) to the data in the previous paper.[2] In case of the addition of organic powders, β was large when the additive

Table IV. The Numerical Values of β, t_i and k_m

Additive	β	t_i(hr)	k_m(hr^{-1})
Absent	1.0	0	1.6×10^{-2}
Vitamin K_3	1.6	0	4.3×10^{-6}
Acridine	1.1	0	6.2×10^{-3}
Methylene blue	1.1	0	4.7×10^{-3}
Phenothiazine	1.0	40	9.4×10^{-3}
p-Hydroquinone	1.5	0	3.7×10^{-5}
Barbituric acid	1.5	0	6.6×10^{-5}
White alundum	1.5	0	5.9×10^{-5}
Silica sands	1.9	0	4.7×10^{-7}
Zinc oxide	1.5	40	2.6×10^{-5}
Barium sulfate	1.4	0	1.0×10^{-4}
Sodium chloride	1.2	12	2.0×10^{-3}
Activated charcoal	0.42	100	2.9×10
Talc	1.0	30	1.6×10^{-2}

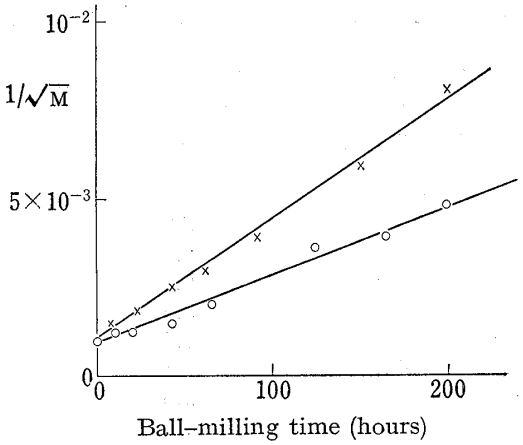

Fig. 11. Application of Equation (2) to Ball-Milling of PVP with 10 w/w% of *p*-Hydroquinone or Barbituric Acid

p-hydroquinone: ○; barbituric acid: ×

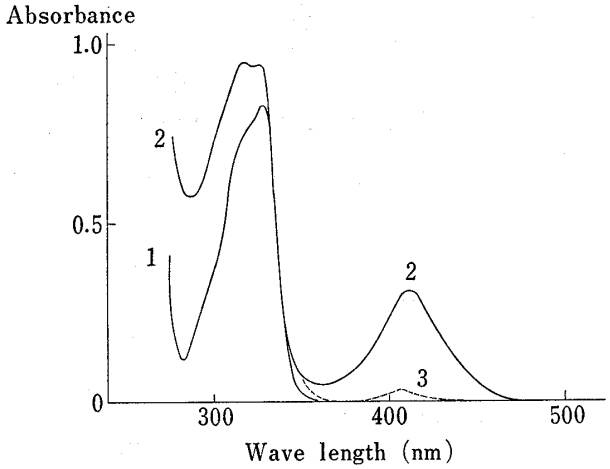

Fig. 12. Influence of Ball-Milling with PVP on UV Spectra of Aqueous Solutions of Barbituric Acid

1: The diluent of 1/21 of an aqueous solution of barbituric acid saturated at 30°
2: 0.173 w/v% of the solution of the mixture of PVP and barbituric acid ball-milled for 200 hours immediately after the preparation
3: 0.173 w/v% of the solution of the mixture of PVP and barbituric acid ball-milled for 200 hours after 24 hours from the time of the preparation

Table V. Elemental Analysis of Ball- Milled PVP

Additive	Ball-milling time (hr)	Content (w/w %)		
		Carbon	Hydrogen	Nitrogen
	0	64.48	7.66	11.72
Chloranil	200	53.08	8.16	10.01
Vitamin K_3	200	55.31	8.19	9.94
Acridine	200	58.25	8.12	11.92
Methylene blue	200	54.50	7.94	10.72
Phenothiazine	200	54.70	8.41	10.18
p-Hydroquinone	200	58.41	7.58	12.90
Barbituric acid	200	58.68	7.39	9.61
White alundum	200	56.74	7.73	10.62
Silica sands	200	56.88	7.87	10.60
Zinc oxide	200	56.91	7.94	9.43
Barium sulfate	200	56.60	7.72	9.24
Sodium chloride	200	54.54	8.14	10.17
Activated charcoal	250	57.83	7.63	10.26
Talc	200	56.30	7.21	10.29

was a poor electron donor. The value of β was large for the case of the addition of hard inorganic powders. In case of the addition of soft inorganic powders, β was small and t_i was larger than zero.

The white mixture of PVP K90 and barbituric acid discolored into yellow by ball-milling only for five hours. As shown in Fig. 12, a new peak was observed at 410 nm in the UV spectrum of the aqueous solution of barbituric acid ball-milled in the presence of PVP. The new peak disappeared by leaving the solution alone for more than 48 hours. The peak at 410 nm was not observed in the spectrum of the solution of original barbituric acid. This phenomenon was not obseved by mixing of original or ball-milled PVP with barbituric acid, or by ball-milling only barbituric acid. It is suggested from these findings that barbituric acid interacts chemically with PVP in the solid state by ball-milling and that the interaction force is weak. But apparent change attributed to the interaction was not observed in the IR spectra of the ball-milled sample of the mixture of PVP and barbituric acid. The above phenomenon was not obseved by ball-milling the mixture of PVP and barbituric acid derivatives, such as barbital.

In order to remove the additive from ball-milled PVP as completely as possible, the cellulose tubing containing the supernatant obtained by centrifugal separation of the aqueous solution of the sample was immersed in distilled water for a week. Then, the purified sample of ball-milled PVP was obtained by freeze-drying of the solution in the cellulose tubing. As shown in Table V, the content of carbon for ball-milled PVP was smaller than that for original PVP. Apparent change was not obtained between IR spectrum of the chloroform solution of the original PVP and those of the ball-milled PVP. But the IR spectra of KBr tablets of the purified samples of PVP ball-milled

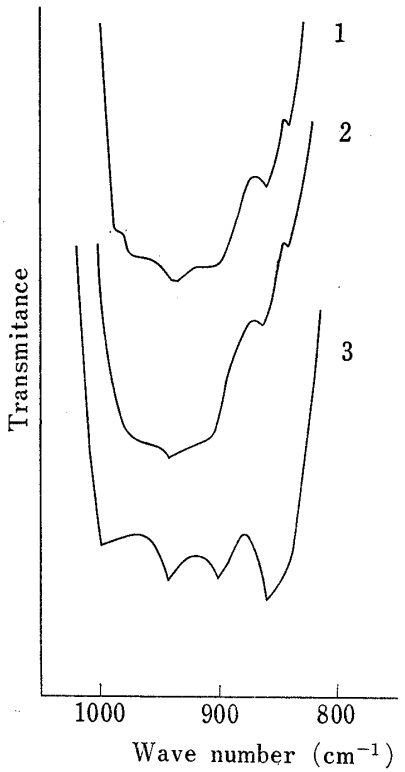

Fig. 13. Influence of Ball-Milling with Additions on IR Spectra of PVP

1: PVP ball-milled with white alundum for 200 hours
2: PVP ball-milled with talc for 200 hours
3: PVP K15

in the presence of white alundum, silica sands, activated charcoal, talc or *p*-hydroquinone seemed to be different from the spectrum of original PVP, as shown in Fig. 13. Kurosaki reported that the absorption at the region between 800 and 1000 cm^{-1} in the IR spectra of 2-pyrrolidone and N-methyl-2-pyrrolidone was due to C-H_2 twisting vibration and C-C streching vibration.[7]

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7) K. Kurosaki, *Nihon Kagaku Zasshi*, **82**, 1691 (1961).