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Induction Period for a Decrease in Molecular Weight of Polyvinylpyrrolidone by Ball-Milling in Various Kinds of Atmosphere in the Presence of Organic and Inorganic Powders

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Polyvinylpyrrolidone (PVP) was ball-milled in nitrogen in the presence of chloranil, vitamin K_3, acridine, phenothiazine, *p*-hydroquinone, barbituric acid, white alundum, silica sands, zinc oxide, sodium chloride, activated charcoal or talc. An induction period of 20—120 hours, at the time when molecular weight of PVP began to decrease, was observed in case of ball-milling PVP in the presence of Vitamin K_3, acridine, phenothiazine, zinc oxide or talc. The induction period was longer than 200 hours in the presence of chloranil or the granules of activated charcoal. The induction period decreased by the presence of oxygen or the small quantity of the vapor of distilled water or the aqueous solution of hydrogen peroxide in the ball-milling atmosphere.

The electron spin resonance (ESR) spectra of the mixtures of PVP and the additive showed that interaction was caused between them by ball-milling. When a large induction period was observed, the intensity of the signal in the ESR spectra increased slightly at the first stage of ball-milling and remarkably by ball-milling after the lapse of the induction period.

The scanning electron microscopic photographs of the ball-milled mixtures suggested that the particles of the additive filled in the pores on the surface of PVP and got into the particles of PVP gradually by ball-milling. The molecular weight and the particle size of PVP seemed to begin to decrease after the particles of the additive filled in the pore thoroughly by ball-milling, when a long induction period was observed.

Keywords——induction period; polyvinylpyrrolidone; ball-milling in the presence of the additive; decrease in molecular weight; ball-milling atmosphere; formation of radicals; interaction of the additive with polyvinylpyrrolidone caused by ball-milling; chloranil; granules of activated charcoal; fine powders of activated charcoal

It was reported in the previous paper that an induction period of more than 100 hours, at the time when molecular weight of polyvinylpyrrolidone (PVP) began to decrease, was observed in case of ball-milling PVP in air in the presence of chloranil or the granules of activated charcoal.[2]

In this paper, PVP was ball-milled in various kinds of atmosphere in the presence of organic and inorganic powders and some discussion was made on the parameters concerning the induction period.

Experimental

The materials used were PVP K90 purchased from Wako Pure Chemicals Industries LTD. and PVP K15 purchased from Daiichi Pure Chemicals Co., LTD. The mean molecular weights of PVP K90 and PVP K15 determined by viscometry were 9.6×10^5 and 7.5×10^3, respectively.[3] The additives used were chloranil, vitamin K_3, acridine, phenothiazine, *p*-hydroquinone, barbituric acid, white alundum (type 40, 1000 and 4000), silica sands, zinc oxide, sodium chloride, talc, and the granules and the fine powders of activated charcoal. Silica sands (type 3) were purchased from Kokusan Chemical Works LTD., the granules of activated charcoal were purchased from Wako Pure Chemicals Industries LTD. and the fine powders of activated charcoal were from Hitachi Carbon Chemicals LTD. Talc purchased from Nihon Talc Co. were crushed,

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

[3] N. Kaneniwa and A. Ikekawa, *Yakuzaigaku*, **31**, 201 (1971).

and the particles smaller than 1 cm in diameter were used in this paper. The mean surface diameters of the particles of type 1000 and 4000 of white alundum were 11.6 and 4.9 μ, respectively, as determined by the air permeability method.[4] The physical and chemical properties of the additives were referred to the previous paper.[2] Hydrogen peroxide (JIS K–8230) purchased from Mitsubishi Gasu Kagaku Co. was the aqueous solution of 30 w/w % of hydrogen peroxide.

A stainless steel mill in the inside diameter of 10 cm and in capacity of 870 ml, and stainless steel balls with true density of 8.2 g/cm^3 and in diameter of 1.9 cm and 2.5 cm were used for ball-milling. The ratio of the number of balls in diameter of 1.9 cm to the number of them in diameter of 2.5 cm was 3.0 in all the experiments in this paper.

Various amounts of the mixture of PVP K90 and each of the additives in various ratios was inserted in the mill containing various amounts of the balls, and the mixture was ball-milled in nitrogen, air, oxygen, in nitrogen or oxygen containing small quantity of the vapor of distilled water or in nitrogen containing small quantity of the vapor of hydrogen peroxide. When the mixture was ball-milled in the atmosphere other than air, the air in the mill was replaced by the other gas, using the apparatus shown in Chart 1. After the air in the mill was exhausted with a vacuum pump, the vapor of distilled water or hydrogen peroxide was introduced into the mill and the pressure of the vapor was measured by a manometer. Then, nitrogen or oxygen was introduced into the mill, until the pressure of the gas in the mill was equilibrated with the atmospheric pressure. In all the experiments, the mill was revolved with the velocity of 0.74 times the critical velocity at which the gravitational force of balls was equal to the centrifugal force given to balls by the revolution of a mill.[5]

Approximately 50 mg of the ball-milled sample was picked out of the mill at intervals and the mean molecular weight of PVP in the sample was measured by viscometry according to the method reported in the previous paper.[2,6] Electron spin resonance (ESR) spectra of the ball-milled powders were measured in air at 23° with an ESR spectrometer (Model JES-PE). X-ray diffraction diagrams of the samples were measured with a JEOL X-ray diffractometer (Model JDX-7E). Heat generated by adding the mixture of PVP and the additive in distilled water and heat of solution of PVP in distilled water were measured with a micro-thermal calorimeter (Model CM-204s1). Scanning electron microscopic photographs of the samples were taken by a Hitachi scanning electron microscope (Model SSM-2).

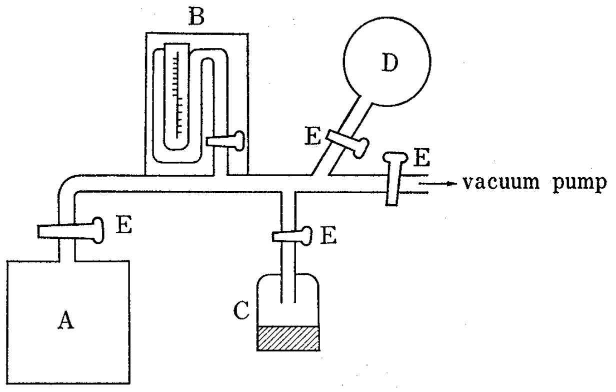

Chart 1. Apparatus for Replacement of Air in a Mill by the Other Gas

A: a stainless steel mill. The lid used is referred to the previous paper.[3]
B: a manometer.
C: the container of distilled water or 30 w/w % of the aqueous solution of hydrogen peroxide.
D: a gum balloon containing nitrogen or oxygen.
E: glass cocks.

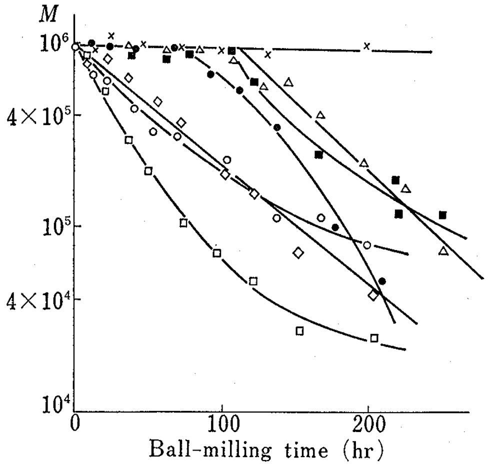

Fig. 1. Decrease in Molecular Weight of PVP, M, by Ball-Milling in Nitrogen in the Presence of 10 w/w % of Organic Additives

W_s=20 g,[a] J_b=0.22.[b]
Additive
×: chloranil.
△: acridine.
◇: p-hydroquinone.
○: absent.
■: vitamin K$_3$.
●: phenothiazine.
□: barbituric acid.

a) W_s: the total weight of the sample inserted in a mill.
b) J_b: the ratio of the apparent volume of the balls in a mill to the capacity of the mill.[5]

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4) N. Kaneniwa, A. Ikekawa, T. Ozaki, C. Shinya, N. Sugimoto, and Y. Hozumi, *Yakugaku Zasshi*, **88**, 1642 (1968).
5) N. Kaneniwa, A. Ikekawa, and K. Hashimoto, *Chem. Pharm. Bull.* (Tokyo), **21**, 676 (1973).
6) N. Kaneniwa and A. Ikekawa, *Chem. Pharm. Bull.* (Tokyo), **20**, 1536 (1972).

Results and Discussion

1) The Induction Period for Ball-milling PVP K90 in Nitrogen in the Presence of Various Kinds of Organic and Inorganic Additives

Fig. 1 shows the influence of organic additives on a decrease in molecular weight of PVP by ball-milling in nitrogen. Approximately 100 hours of the induction period was observed in the presence of vitamin K_3, acridine or phenothiazine, and an appreciable decrease in molecular weight of PVP was not observed even after ball-milling for 200 hours in the presence of chloranil. The rate of a decrease in molecular weight of PVP at the first stage of ball-milling was larger in the presence of barbituric acid than in the presence of the other powders or in the absence of the additives.

Fig. 2 shows the influence of inorganic additives on a decrease of molecular weight of PVP by ball-milling in nitrogen. As reported in the previous paper, the particles of white alundum are very hard and Mohrse's hardness of the powders decreases in the order of white alundum, silica sands, zinc oxide, sodium chloride, activated charcoal and talc.[2] Approximately 30 hours of the induction period was observed in the presence of soft powders, and an appreciable decrease in molecular weight of PVP was not observed even after ball-milling for 200 hours in the presence of the granules of activated charcoal. The rate of a decrease in molecular weight of PVP at the first stage of ball-milling was larger in the presence of white alundum than in the presence of the other additives or in the absence of the additives.

As reported in the previous paper, the white mixture of PVP and barbituric acid turned into yellow by ball-milling in air. A new peak appeared at 410 nm in the absorption spectrum of an aqueous solution of the mixture by ball-milling in air immediately after the preparation, and the new peak disappeared gradually on standing.[2] The same phenomenon was also observed in case of ball-milling the mixture in nitrogen. On the other hand, a new signal appeared around 44.6° of 2θ in the X-ray diffraction diagram of white alundum by

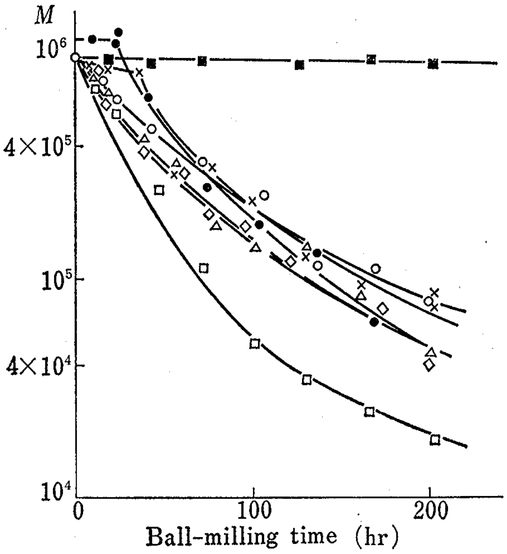

Fig. 2. Decrease in Molecular Weight of PVP, M, by Ball-Milling in Nitrogen in the Presence of 10 v/v % of Inorganic Additives by True Volume

W_s=20 g, J_b=0.22

Additive.

□: white alundum (type 40). △: silica sands.

×: zinc oxide. ◇: sodium chloride.

■: granules of activated charcoal.

●: talc ○: absent.

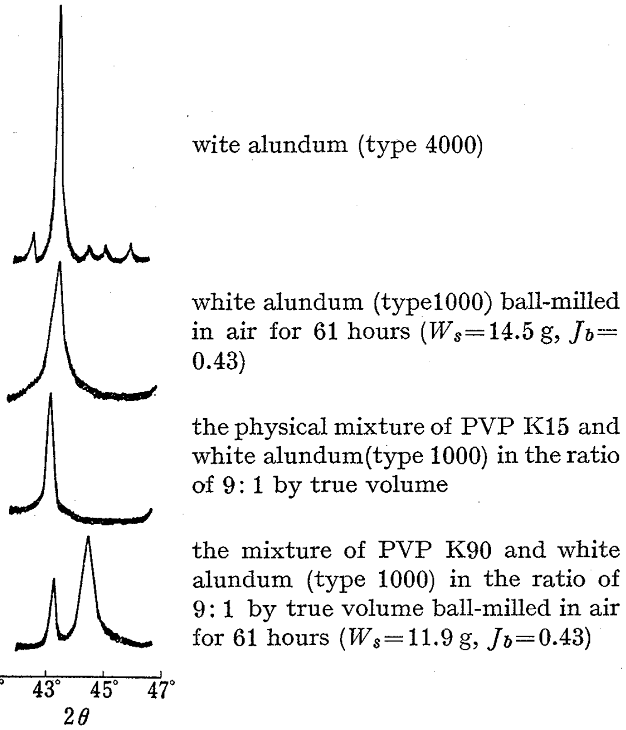

Fig. 3. Influence of Ball-Milling in the Presence of PVP on X-Ray Diffraction Digrams of White Alundum

ball-milling in the presence of amorphous PVP (Fig. 3). The new signal was not observed by ball-milling white alundum alone. The similar phenomenon was not found in the presence of the other inorganic additives. These phenomena may be related to the finding that the rate of a decrease in molecular weight of PVP at the first stage of ball-milling is large in the presence of barbituric acid or white alundum.

The rate of a decrease in molecular weight of PVP by ball-milling in nitrogen in the presence of various kinds of the additive was compared with the rate in air reported in the previous paper.[2] As shown in Fig. 4, the rate in the presence of vitamin K_3 or phenothiazine was larger in nitrogen than in air. In the presence of the other additives, the rate was not influenced remarkably by the ball-milling atmosphere.

Approximately, equation (1) was applied to a decrease in molecular weight of PVP by ball-milling, where M was the molecular weight of PVP ball-milled for t hours determined by viscometry, t_i was an induction period at the time when molecular weight of PVP began to decrease, and k and β were parameters dependent on the ball-milling atmosphere, physical and chemical properties of the additive and so on (Fig. 5).

$$\begin{aligned} t &\leq t_i \qquad -dM/dt = 0 \\ t &> t_i \qquad -dM/dt = k\cdot M^{\beta} \qquad (1) \end{aligned}$$

The numerical values of the parameters, β, k and t_i are tabulated in Table I. The values for ball-milling in air were quoted from the previous paper for comparison of them with the values in nitrogen.[2] In case of ball-milling PVP in the presence of the granules of activated charcoal in air, β was considered to be equal to or below 1.0, though the number of the data of the molecular weight of PVP at the ball-milling time after the induction period was too small for the values of the parameters to be obtained accurately. In this case, the values of t_i and k were obtained under the assumption that β was 1.0 (Table I).

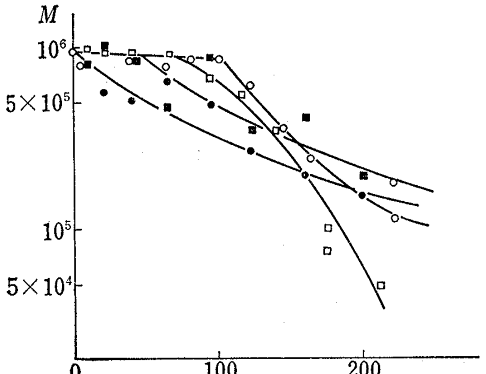

Fig. 4. Influence of Ball-Milling Atmosphere on a Decrease in Molecular Weight of PVP, M, in the Presence of Vitamin K_3 and Phenothiazine

$W_s=20$ g, $J_b=0.22$.
The content of vitamin K_3 and phenothiazine in the mixture with PVP; 10 w/w %.

Additive	Atmosphere	Symbol
Vitamin K_3	Nitrogen	○
Vitamin K_3	Air	●
Phenothiazine	Nitrogen	□
Phenothiazine	Air	■

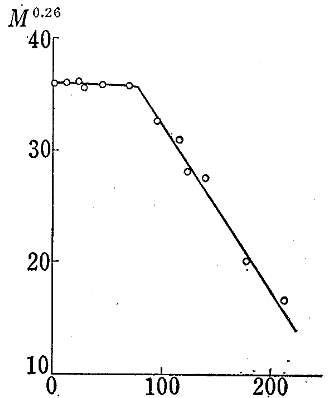

Fig. 5. Application of Equation (1) to a Decrease in Molecular Weight of PVP, M, by Ball-Milling in Nitrogen in the Presence of 10 w/w % of Phenothiazine

$W_s=20$ g, $J_b=0.22$.

The value of β was influenced little by the ball-milling atmosphere in the presence of organic additives. The value of β in the presence of acridine or phenothiazine was a little smaller and the value in the presence of vitamin K_3 and barbituric acid was a little larger than the value in the absence of the additives. In case of ball-milling in air, the value of β in

Table I. Numerical Values of β, k and t_i for Ball-Milling PVP in the Presence of Organic or Inorganic Additives

Additive	Atmosphere	β	k (hr^{-1})	t_i (hr)
Vitamin K_3	Nitrogen	1.4	1.4×10^{-4}	104
	Air	1.6	4.3×10^{-6}	0
Acridine	Nitrogen	1.0	1.8×10^{-2}	115
	Air	1.1	6.2×10^{-3}	0
Phenothiazine	Nitrogen	0.74	5.0×10^{-1}	70
	Air	1.0	9.4×10^{-3}	40
p-Hydroquinone	Nitrogen	1.0	1.6×10^{-2}	0
	Air	1.5	3.7×10^{-5}	0
Barbituric acid	Nitrogen	1.4	2.1×10^{-4}	0
	Air	1.5	6.6×10^{-5}	0
White alundum (type 40)	Nitrogen	1.3	6.7×10^{-4}	0
	Air	1.5	5.9×10^{-5}	0
Silica sands (type 3)	Nitrogen	1.3	3.1×10^{-4}	0
	Air	1.9	4.7×10^{-7}	0
Zinc oxide	Nitrogen	1.4	9.3×10^{-5}	35
	Air	1.5	2.6×10^{-5}	40
Sodium chloride	Nitrogen	1.3	3.3×10^{-4}	0
	Air	1.2	2.0×10^{-3}	12
Granules of activated charcoal	Air	1.0	2.4×10^{-2}	147
Talc	Nitrogen	1.4	2.1×10^{-4}	24
	Air	1.0	1.6×10^{-2}	30
Absent	Nitrogen	1.3	3.0×10^{-4}	0
	Air	1.0	1.6×10^{-2}	0

Content of the organic additives; 10 w/w %.
Content of the inorganic additives; 10 v/v % by true volume.
$W_s=20$ g, $J_b=0.22$.

the presence of hard inorganic powders was a little larger than the value in the presence of soft inorganic powders or in the absence of the additives. When PVP was ball-milled in nitrogen, β was influenced little by the addition of the inorganic powders. When PVP was ball-milled in the presence of vitamin K_3 or acridine, the value of t_i in nitrogen was much larger than the value in air.

2) Influence of the Ball-milling Atmosphere on the Induction Period for the Mixtures of Chloranil or the Granules of Activated Charcoal

Fig. 6 and 7 show a decrease in molecular weight of PVP by ball-milling in various kinds of atmosphere in the presence of 5 w/w % of chloranil and 10—15.1 w/w % of activated charcoal, respectively. In Table II and III are shown the values of the parameters, β,k and t_i obtained for the results in Fig. 6 and 7. In case of the addition of chloranil, an appreciable decrease in molecular weight of PVP was not observed even after ball-milling for 134 hours in nitrogen. But t_i was around 45 hours in the atmosphere containing oxygen or small quantity of the vapor of distilled water or the aqueous solution of hydrogen peroxide. The value of t_i seemed to be a little small in the atmosphere containing oxygen of partial pressure of approximately 1.0. But k and β were influenced little by the ball-milling atmosphere other than nitrogen. Ten grams of chloranil was ball-milled in air for 60 hours in the absence of PVP under the same condition in Fig. 6. The value of t_i obtained by adding the ball-milled chloranil was identical with the value obtained by adding the original chloranil. But, when the ball-milled chloranil was added, β seemed to be a little smaller than the value obtained by adding the original chloranil.

It was considered from Fig. 7 and Table III that t_i was influenced little by the content of the granules of activated charcoal in the mixture with PVP when the content was between 10 and 15.1 w/w %. Accordingly, it was considered that t_i decreased by the presence of oxygen or small quantity of the vapor of distilled water or the aqueous solution of hydrogen peroxide. But t_i increased with an increase in the partial pressure of oxygen in the atmosphere other than nitrogen. The value of β for the case of ball-milling in the presence of the granules of activated charcoal in oxygen containing small quantity of the vapor of distilled water was large, but the value was 1.0 in the other atmosphere, though the parameters in nitrogen could not be obtained. The value of k was small in nitrogen containing small quantity of the vapor of the aqueous solution of hydrogen peroxide. In case of the addition of fine powders of activated charcoal, t_i was negligibly small.

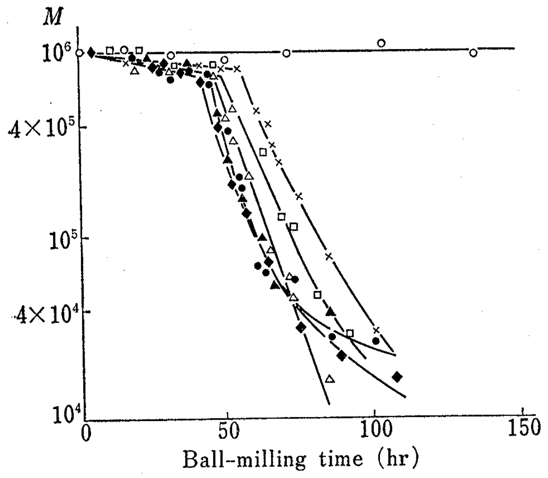

Fig. 6. Decrease in Molecular Weight of PVP, M, by Ball-Milling in the Presence of 5 w/w % of Chloranil in Various Kinds of Atmosphere

$W_s=10$ g, $J_b=0.43$

Atmosphere.

○: N_2 ●: $N_2(H_2O)$[a] ×: $N_2(H_2O_2)$[a]
□: air △: air[b] ▲: O_2
◆: $O_2(H_2O)$[a]

a) Referred to Table II.

b) In this case, the mixture of PVP K90 and the ball-milled chloranil was ball-milled, though the mixture of original chloranil was ball-milled in the other cases.

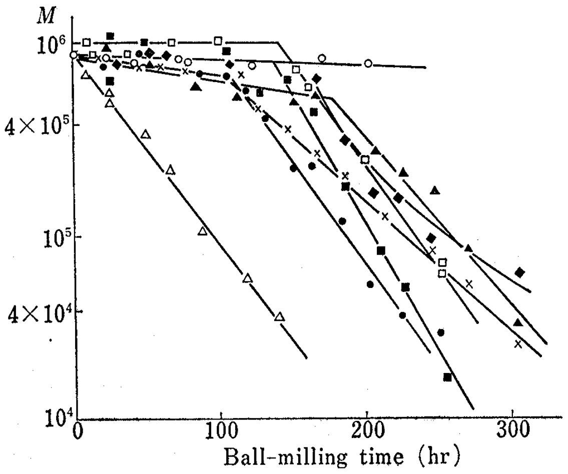

Fig. 7. Decrease in Molecular Weight of PVP, M, by Ball-Milling in the Presence of Activated Charcoal (AC) in Various Kinds of Atmosphere

Atmosphere	Kind of AC	Content of AC (w/w %)	Symbol
N_2	Granules	15.1	○
$N_2(H_2O)$[a]	Granules	10	●
$N_2(H_2O_2)$[a]	Granules	10	×
Air	Granules	10	■
Air	Granules	15.1	□
Air	Fine powders	10	△
O_2	Granules	15.1	▲
$O_2(H_2O)$[a]	Granules	10	◆

a) Referred to Table III.

TABLE II. Numerical Values of β, k and t_i for Ball-Milling PVP in the Presence of 5 w/w % of Chloranil in Various Kinds of Atmosphere

$W_s=10$ g, $J_b=0.43$

Kind of chloranil	Atmosphere	β	k (hr^{-1})	t_i (hr)
Original	$N_2(H_2O)$[a]	1.19	4.3×10^{-3}[d]	45
Original	$N_2(H_2O_2)$[b]	1.14	3.8×10^{-3}[d]	56
Original	Air	1.20	3.8×10^{-3}[d]	47
Ball-milled	Air	1.00	9.6×10^{-2}	45
Original	O_2	1.25	3.8×10^{-3}[d]	37
Original	$O_2(H_2O)$[c]	1.27	3.8×10^{-3}[d]	37

a) In nitrogen containing H_2O of the vapor pressure of 22 mmHg.

b) In nitrogen containing 30 w/w % aqueous solution of hydrogen peroxide of the vapor pressure of 13 mmHg.

c) In oxygen containing H_2O of the vapor pressure of 22 mmHg.

d) The mean value of all the data of β for original chloranil was 1.25. The values of k in this Table were calculated under the assumption that β was 1.25.

Table III. Numerical Values of β, k and t_i for Ball-Milling PVP in the Presence of Activated Charcoal (AC) in Various Kinds of Atmosphere
$W_s=20$ g, $J_b=0.22$

Content of AC (w/w %)	Kind of AC	Atmosphere	β	k (hr^{-1})	t_i (hr)
10	Granules	$N_2(H_2O)$[b]	1.0	2.7×10^{-2}	110
10	Granules	$N_2(H_2O_2)$[c]	1.0	1.7×10^{-2}	107
10	Granules	Air	1.0	3.2×10^{-2}	131
15.1[a]	Granules	Air	1.0	2.6×10^{-2}	147
10	Fine powders	Air	1.0	2.5×10^{-2}	0
15.1[a]	Granules	O_2	1.0	2.4×10^{-2}	192
10	Granules	$O_2(H_2O)$[d]	2.0	1.0×10^{-7}	167

a) 15.1 w/w % = 10 v/v % by true volume (when activated charcoal is added).
b) In nitrogen containing H_2O of the of the vapor pressure of 17 mmHg.
c) In nitrogen containing 30 w/w % aqueous solution of hydrogen peroxide of the vapor pressure of 15 mmHg.
d) In oxygen containing H_2O of the vapor pressure of 16 mmHg.

3) Influence of the Content of Chloranil in the Mixture with PVP K90 on the Induction Period

Fig. 8 shows the influence of the content of chloranil in the mixture with PVP on a decrease in molecular weight of PVP by ball-milling the mixture. In Table IV are tabulated the values of β, k and t_i for the results in Fig. 8. The values of β and k were influenced little by the content of chloranil when the content was below 10 w/w %. When the content was above 20 w/w %, β was large and the rate of a decrease in molecular weight of PVP by ball-milling was small, though the values of the parameters for the case of 20 w/w % of the content could not be obtained. When the content was below 10 w/w %, t_i was proportional to the content raised to the power 1.8, but the value of t_i in case of the content above 20 w/w % was smaller than the value in case of the content between 10 and 20 w/w %. It was reported in the previous paper that interaction was caused between PVP and chloranil in the solid

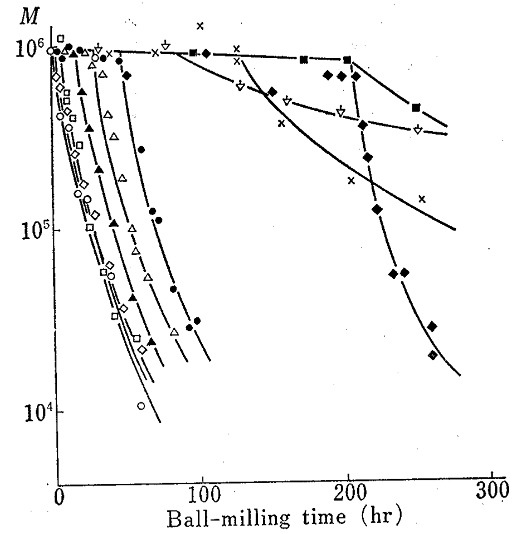

Fig. 8. Influence of the Content of Chloranil in the Mixture with PVP on a Decrease in Molecular Weight of PVP, M, by Ball-Milling

$W_s=10$ g, $J_b=0.43$.
Content of chloranil (w/w %).
○: 0 ◇: 0.51 □: 1.1 ▲: 2.0 △: 3.6
●: 5.0 ◆: 10 ■: 20 ☆: 40 ×: 70

Table IV. Numerical Values of β, k and t_i for Ball-Milling PVP in Air in the Presence of Various Amounts of Chloranil
$W_s=10$ g, $J_b=0.43$

Cotent of chloranil (w/w %)	β	k (hr^{-1})	t_i (hr)
0	1.21	4.5×10^{-3}[a]	0
0.51	1.23	3.5×10^{-3}[a]	1.5
1.1	1.37	4.3×10^{-3}[a]	4
2.0	1.26	4.5×10^{-3}[a]	18
3.6	1.41	4.3×10^{-3}[a]	33
5.0	1.20	3.8×10^{-3}[a]	47
10	1.21	4.8×10^{-3}[a]	210
20	—	—	200—250
40	1.6	2.4×10^{-6}	80
70	1.7	2.1×10^{-6}	130

a) When original chloranil was added to PVP, the mean value of β in case of the weight content of chloranil below 10 w/w % was 1.25. In this Table, the values of k were calculated under the assumption that β was 1.25.

state by ball-milling.⁷⁾ It is expected that the interaction between PVP and chloranil becomes more remarkable with an increase in the content of chloranil when the amount of chloranil is much smaller than that of PVP. Conversely, it is probable that the interaction becomes more remarkable with an increase in the content of PVP when the amount of PVP is much smaller than that of chloranil. Fig. 8 and Table IV seem to suggest that the induction period is influenced by the interaction between PVP and the additive caused by ball-milling.

Heat generated by adding the mixture of PVP and the additive into distilled water was measured. As shown in Table V, heat for the ball-milled mixture of chloranil was larger than the heat for the physical mixture. It was reported in the previous paper that PVP interacted with acridine in the aqueous solution and that the interaction was remarkable for PVP of low molecular weight.⁷⁾ The heat for the physical mixture of PVP K15 and acridine was larger than the heat for the physical mixture of PVP K90. The heat for the ball-milled mixture of acridine seemed to be larger than the heat for the physical mixture of PVP K15. It is suggested that an increase in the heat for the ball-milled mixtures of chloranil or acridine is attributed to their interaction with PVP caused by ball-milling. But, for the other cases, remarkable difference was not observed between them as the example shown in TableV.

TABLE V. Heat Generated by Adding the Mixture of PVP and an Additive to Distilled Water, H_m, and Heat of Solution of PVP in Distilled Water, H_s

Type of PVP	Additive	Content of additive (w/w %)	Ball-milling time (hr)	Ball-milling atmosphere	Molecular weight of PVP	H_m cal/g of the mixture	$H_s$$^{a)}$ kcal/mole of PVP (monomer unit)
K90	b-Chloranil$^{b)}$	5	0		9.6×10^5	−36	−4.3
K15	b-Chloranil	5	0		7.5×10^3	−36	−4.3
K90	Chloranil	5	134	Nitrogen	8.6×10^5	−52	−6.2
K90	Chloranil	10	206	Nitrogen	9.7×10^5	−40	−5.1
K90	Chloranil	10	200	Air	1.1×10^6	−46	−5.8
K90	Chloranil	5	98	Air	3.2×10^4	−47	−5.6
K90	Vitamin K_3	10	0		9.6×10^5	−39	−4.9
K15	b-Vitamin K_3	10	0		7.5×10^3	−44	−5.6
K90	Vitamin K_3	10	251	Nitrogen	1.1×10^5	−44	−5.6
K90	Vitamin K_3	10	200	Air	1.5×10^5	−42	−5.3
K90	b-Acridine	10	0		9.6×10^5	−31	−3.9
K15	Acridine	10	0		7.5×10^3	−42	−5.3
K15	b-Acridine	11	0		7.5×10^3	−41	−5.2
K90	Acridine	10	251	Nitrogen	7.5×10^4	−53	−6.7
K90	Acridine	10	207	Air	2.6×10^4	−47	−5.9
K90			0		9.6×10^5		−6.2
K30			0		4.0×10^4		−5.6
K90			420	Nitrogen	2.1×10^4		−5.2
K90			420	Air	2.2×10^4		−5.2
K90			420	Oxygen	2.0×10^4		−5.2
K15			0		7.5×10^3		−4.5

a) The value of H_s for the mixture was calculated under the assumption that H_m was identical with heat of solution of PVP and that PVP in the mixture contained 20 w/w % of water.
b) For example, b-chloranil means ball-milled chloranil.

4) ESR Spectra of the Mixtures of PVP K90 and the Additive

In our previous paper, a signal was observed in the electron spin resonance (ESR) spectrum of the powders of the ball-milled mixture of PVP and chloranil.⁷⁾ On the other hand, several workers reported that chain scission occurred and free radicals were formed

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7) N. Kaneniwa and A. Ikekawa, *Chem. Pharm. Bull.* (Tokyo), 23, 2973 (1975).

by the mechanical treatment of the polymers such as polyethylene terephthalate.[8] Butyagin, et al. also reported that activated points of a radical type were formed at the surface of the solid of silica sands, graphite and others by scission of their covalent bonds by mechanical treatment.[9] Then, ESR spectra of the ball-milled samples were investigated.

Fig. 9 and 10 show the variation of the signals in the ESR spectra of the mixtures of the granules or the fine powders of activated charcoal by ball-milling. No signal was observed in the ESR spectra of the original PVP K90 and PVP K90 ball-milled in the absence of the additive for the time less than or around 200 hours. The signal in the ESR spectra of the fine powders of activated charcoal before ball-milling was similar to the signal for the physical mixture with PVP K90 in Fig. 10, and the signal seemed to be the superposition of a narrow signal and a broad signal. But no signal was observed in the spectra of the granules of activated charcoal before and after ball-milling in the absence of PVP, the fine powders of activated charcoal ball-milled in the absence of PVP and the mixtures of them with PVP. In Fig. 9 and 10, the intensity of the signal for the mixtures of activated charcoal increased remarkably by ball-milling. This phenomenon was considered to be attributed to the interaction of activated charcoal with PVP by ball-milling.

The similar phenomenon was also observed for the case of the mixtures of the organic additives. No signal was observed in the spectra of the physical mixtures of PVP K90 and acridine, or *p*-hydroquinone. But a large signal was observed in the spectra of these mix-

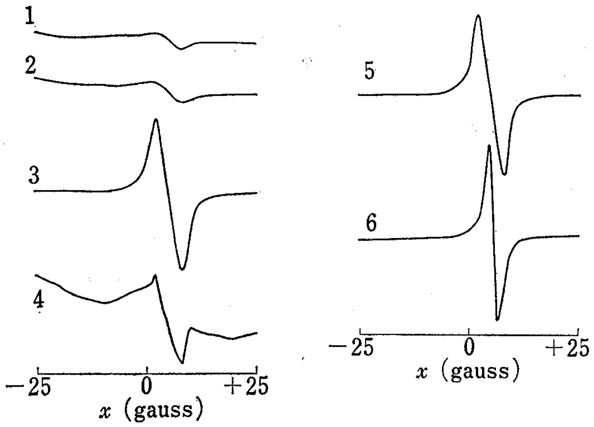

Fig. 9. Influence of Ball-Milling in Air on the ESR Spectra of the Mixtures of PVP K90 and the Granules of Activated Charcoal in the Ratio of 9:1 by Weight

Ball-milling condition; $W_s=20$ g, $J_b=0.22$.

Measurement was made by inserting in a sample tube of quartz glass in diameter of 4 mm a Pyrex tube containing the powders of the sample.

Field: 3360 ± x gauss.

	Ball-milling time (hr)	the Diameter of the Pyrex tube (mm)	Modulation width (gauss)	Amplitude
1	24	1.1	0.63×10	$10\ \times10^2$
2	104	1.1	0.63×10	$10\ \times10^2$
3	146	1.1	0.63×10	2.5×10^2
4	146	0.8	0.63×10	5.0×10^2
5	163	0.8	0.63×10	3.2×10^2
6	271	0.8	$0.63\times\ 1$	2.0×10^2

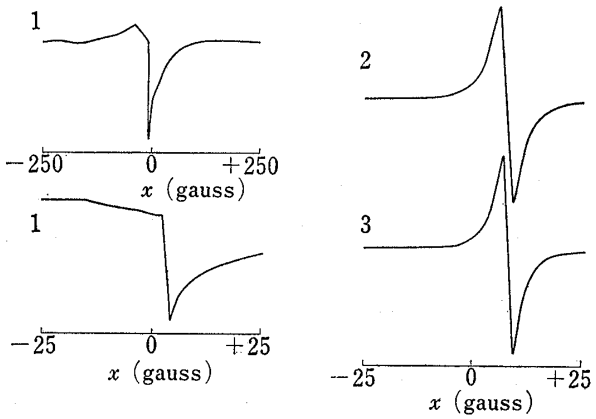

Fig. 10. Influence of Ball-Milling in Air on ESR Spectra of the Mixtures of PVP K90 and the Fine Powders of Activated Charcoal in the Ratio of 9:1 by Weight

Ball-milling condition; $W_s=20$ g, $J_b=0.22$.

Field; 3360 ± x gauss, Modulation width; 0.63×1 gauss.

	Ball-milling time (hr)	The diameter of the Pyrex tube (mm)	Amplitude
1	0	4[a]	5.0×10^2
2	22	0.8	5.6×10
3	113	0.8	$2.5\times\ 1$

a) The ESR spectra of the ball-milled samples were measured by the same way as mentioned in Fig. 9, but the spectra of the physical mixture were measured by inserting the sample directly in a sample tube.

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8) V.A. Zakrevskii, E.E. Tomashevskii, and V.V. Baptizmanskii, *Vysokomol. Soedin. Ser. B*, **10** (3), 193 (1968); A. Peterlin, *J. Phys. Chem.*, **75**, 3921 (1971); G.A. Gorokhovskii, P.A. Chernenko, V.A. Vonsyatskii and I.A. Popov, *Dokl. Akad. Nauk SSSR* [*Phys. Chem.*], **204** (1), 126 (1972); T.C. Chiang and J.P. Sibilia, *J. Polym. Sci. Polym. Phys.*, **10**, 2249 (1972).

9) P. Yu. Butyagin, A.A. Berlin, A.E. Kalmanson, and L.A. Blyumenfel'd, *Vysokomolekulyarnye Soedineniya*, **1**, 865 (1959).

tures ball-milled approximately for 200 hours. The intensity of the signal for the mixture of chloranil, vitamin K_3 or phenothiazine ball-milled approximately for 200 hours was much larger than the intensity for their physical mixtures. The same phenomenon was not observed by ball-milling the organic additive in the absence of PVP. It is also considered that an increase in the intensity of the signal for the mixtures of organic additives by ball-milling is due to the interaction of the additives with PVP caused by ball-milling.

No signal was observed in the ESR spectra of the mixture of white alundum or silica sands. In case of the mixtures of the other inorganic additives before and after ball-milling, no signal was observed or the intensity of the signal was negligibly small.

It was shown from the above facts that a large induction period was observed when the intensity of the signal in the ESR spectra of the mixture of PVP and the additive increased remarkably by ball-milling. But, in case of the addition of the fine powders of activated charcoal, p-hydroquinone or barbituric acid, the induction period was not observed or negligibly short, though the intensity of the signal for them increased remarkably by ball-milling. Then, variation of the intensity of the signal for the mixture of the granules of activated charcoal by ball-milling was compared with the variation for the mixture of the fine powders of activated charcoal. As shown in Fig. 10, the broad signal in the spectra of the mixture of the fine powders disappeared and the intensity of the narrow signal increased remarkably at the first stage of ball-milling. The induction period for the mixture of the granules under the condition in Fig. 9 was approximately 131 hours. The intensity of the signal was small for the mixture of the granules ball-milled for less than 100 hours, but after the lapse of the time around the induction period, the intensity increased remarkably with the lapse of the ball-milling time. The similar phenomenon was also observed for the mixtures of the granules of activated charcoal ball-milled in the atmosphere other than air. It is suggested from the above findings that a large induction period is observed when formation of radicals is negligible at the first stage of ball-milling, and the formation becomes remarkable after the lapse of the several period of the time. More details will be reported in a separate paper concerning this phenomenon.

According to the molecular orbital theory, chloranil and vitamin K_3 are good electron acceptors, and phenothiazine is a good electron donor. Acridine is not only an electron acceptor but an electron donor. On the contrary, *p*-hydroquinone and barbituric acid are neither electron acceptors nor electron donors.[10] It is suggested that formation of radicals is influenced by an electron transfer between PVP and the additive by ball-milling.

5) The Scanning Electron Microscopic Photographs of the Ball-milled Mixtures of PVP and the Additive

Fig. 11 shows the variation of the surface state of PVP K90 by ball-milling in the absence of the additive. The particles of original PVP K90 had many pores of comparatively large size on the surface and they were considered to have a sponge-like structure. The size of the pore on the surface decreased and the surface became rough by ball-milling for less than 100 hours, though the surface of the particles ball-milled for 420 hours seemed to be comparatively smooth.

It was considered that the scanning electron microscopic photographs of the ball-milled mixtures showed the surface of the PVP particles, for the particles in the photographs were some of the particles of approximately similar size and shape to which a large part of the particles in the microscopic image at low magnification belonged and the total volume of PVP was approximately nine times of that of the additive. Fig. 12 shows the variation of the surface state of the particles of the mixture of the fine powders of activated charcoal.

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[10] K. Hirano, "Bunshi Seibutsugaku Nyumon," Hirokawa Shoten, Tokyo, 1966, p. 31.

The surface of the particles in Fig. 12 was smooth in comparison with the surface of the particles in Fig. 11 at the first stage of ball-milling.

Fig. 13 and 14 show the variation of the surface of the particles of the mixture of the granules of activated charcoal or chloranil by ball-milling, respectively. In these cases, a long induction period was observed for a decrease in molecular weight of PVP, and the induc-

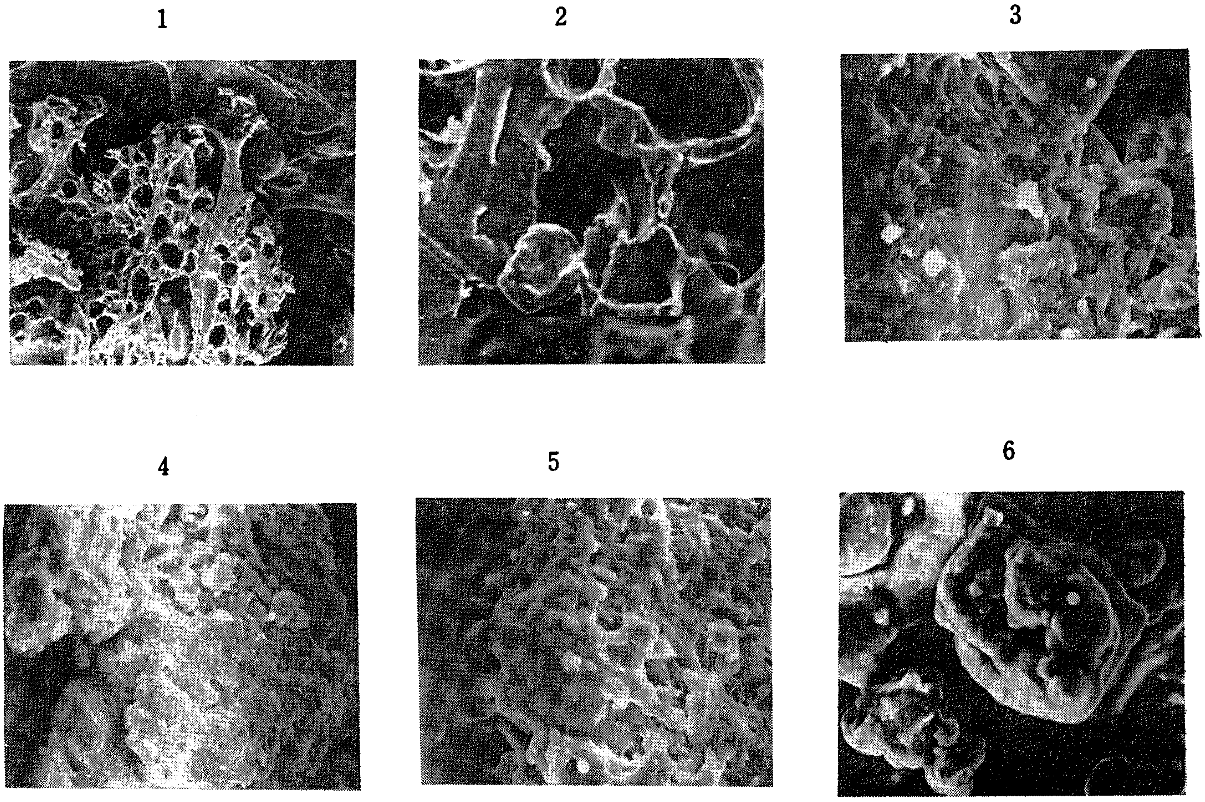

Fig. 11. Scanning Electron Microscopic Photographs of PVP K90

Original PVP K90 Magnification; 1 ×160, 2 ×800.
PVP K90 ball-milled in air (W_s=20 g, J_b=0.22).

	Ball-milling time (hr)	Magnification
3	3	×1000
4	15	×1000
5	102	×1000
6	420	×1600

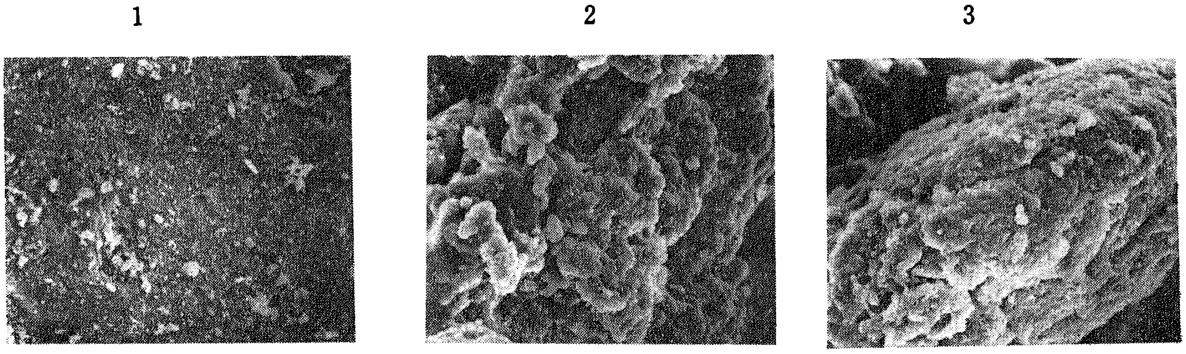

Fig. 12. Scanning Electron Microscopic Photographs of the Ball-Milled Mixtures of PVP K90 and Fine Powders of Activated Charcoal in the Ratio of 9: 1 by Weight

Ball-milling atmosphere; Air, W_s=20 g, J_b=0.22.

	Ball-milling time (hr)	Magnification
1	8	×1000
2	46	×1000
3	83	×1000

tion period was 147 hours under the condition in Fig. 13, and 210 hours under the condition in Fig. 14. The original particles of PVP K90 were flakes of approximately 3—4 mm in size in the long axis. The particle size of PVP K90 decreased slightly by ball-milling for the time below the induction period, and after the lapse of the induction period, the particle size decreased remarkably with the lapse of the ball-milling time. In Fig. 13 and 14, the

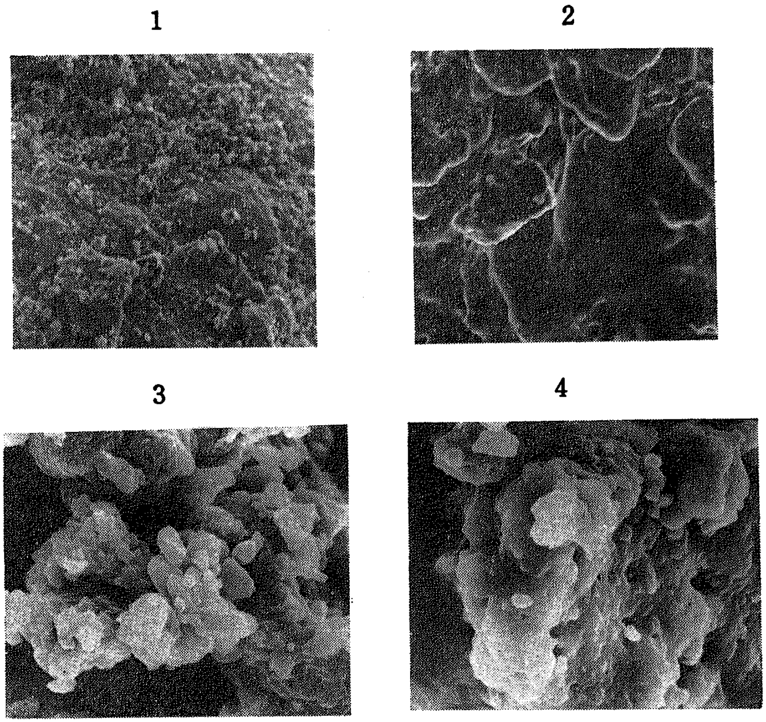

Fig. 13. Scanning Electron Microscopic Photographs of the Mixtures of PVP K90 and the Granules of Activated Charcoal Ball-Milled in Air

The content of activated charcoal: 10 v/v % (by true volume) $J_b=0.22$. The true volume of the mixture inserted in the mill was equal to the true volume of 20 g of PVP.

	Ball-milling time (hr)	Magnification
1	35	× 800
2	130	×1600
3	164	×3000
4	250	×3000

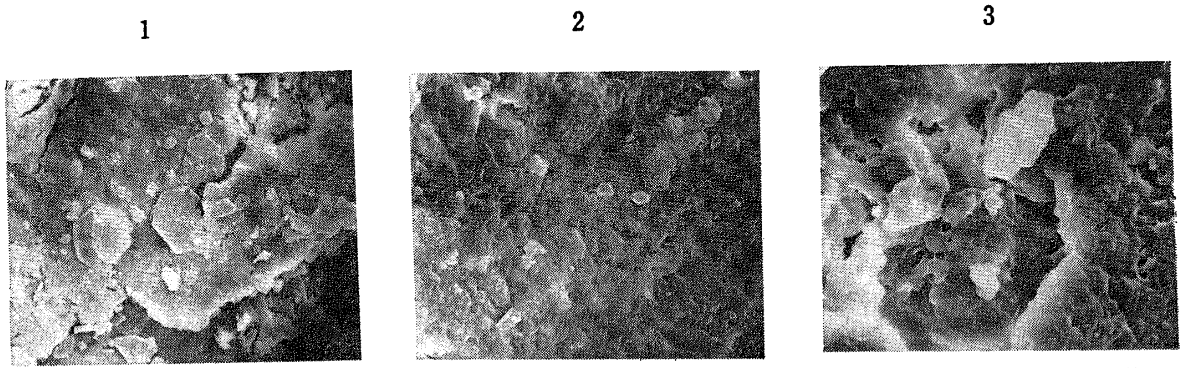

Fig. 14. Scanning Electron Microscopic Photographs of the Mixtures of PVP K90 and Chloranil Ball-Milled in Air

The weight content of chloranil: 10 w/w %, $W_s=10$ g, $J_b=0.43$.

	Ball-milling time (hr)	Magnification
1	25	×1000
2	201	×1000
3	261	×3000

particles of the additive seemed to adhere to the surface of PVP particles at the first stage of ball-milling, but few of these particles were observed and the surface of PVP particles was smooth around the induction period. Few of the small particles which dispersed separately from the particles of PVP were observed in the electron microscopic image at low magnification.

The surface of the ball-milled particles of the mixture of white alundum, zinc oxide, sodium chloride, vitamin K_3 or acridine was smooth compared with the surface of PVP ball-milled in the absence of the additive.

Acridine and vitamin K_3 were soluble in benzene and carbon tetrachloride, but they dissolved slightly in these solvents from the ball-milled mixture with PVP. They dissolved in these solvents by shaking the mixture of the aqueous suspension of the ball-milled mixture and these solvents.7) The dissolution rate of the slightly soluble organic powders in distilled water from the ball-milled mixture with PVP was extremely large in comparison with the rate from the physical mixtures.7) It is suggested from the above findings that the particles of the additive fill in the pore on the surface of PVP K90 and get into the particles of PVP gradually by ball-milling. It seems to be probable that the molecular weight and the particle size of PVP begin to decrease after the particles of the additive fill in the pore on the surface of PVP thoroughly by ball-milling, when a long induction period is observed.

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