

COATED LIMESTONE IN PVC PRODUCTS

S. MIHAJLOVIC*, M. PETROV, Z. SEKULIC, D. RADULOVIC

*Institute for Technology of Nuclear and other Mineral Raw Materials,
Franshet d' Esperey 86, 11000 Belgrade, Serbia and Montenegro*

(Received 14 July 2005; accepted 18 September 2005)

Abstract

Laboratory researches of possibilities of getting coated limestone which is using like filler and producing PVC products was in two phases:

- first phase is getting coated limestone*
- second phase is checking the degree of coating*

Like a start row material was used the limestone from the deposit "Vencac"- Arandjelovac. The results of the experimental researches showed very successfully coating the surfaces of the particles by stearic acid (content 3 %) is making in vibration mill with rings, during which is releasing the degree of coating min 95 %.

Checking the degree of coating is made by microscope way and immersion method (immersion of waters).

Key words: *limestone, filler, coating, PVC products.*

Corresponding author: *s.mihajlovic@itnms.ac.yu*

1. Introduction

Under the term filler in technology of preparing PVC we imply very cheap non-organic materials, from which issue their first task, and it is decreasing the price of total mixture, apropos finished product (1).

Mineral fillers, one of them is CaCO_3 its bigger application find in industry of thermoplastic masses, especially PVC where it has the biggest application.

Industry for producing PVC has same special requests for the quality which are for all the fillers, for CaCO_3 too and it is:

- filler must persist the temperature without any changes. pressure, mechanic tension and all other conditions which are following preparing PVC.
- filler must have easy dispersion of its particulars
- it must be white , without impurities and strange materials
- it mustn't act abrasively
- they mustn't have more then 0.4% of moisture,
- no matter fillers for PVC are non active we need to make accent on the need for their inertion, and compatibility with all additions presented in alloy
- CaCO_3 , like the others non organic fillers we add to PVC always in form fine, dry dust, in the phase of mixing PVC with all other additives, with target for better homogenisation.

Justification of using carbonate rocks like a filler lies in their wide diffusion in the surface, available part of the earth shell, volume of appearing and relatively easy dusting (2).

The requests of preparing industry for some carbonate fillers influence on searching the laboratory solutions of a problem of arrangement of the fine micronized carbonate fillers with oily acids and their salts.

The latest directions of the development are directed to more bigly application of treated limestones, apropos activated limestones. The most often for the activation we use the oily acids, different oils, salts of non oil acids, from the most we use stearic acid and Ca-stearate. By procedure of hemi sorption, on the surface of all particulars of filler origin the mononuclear film of stearate and it is such chemistry bonded and it became the additional

part of every particle. The quantity of such used stearic acid is in the lines 1-3 % (3) .

Interaction between the ion of calcium and neighbour atom oxygen which belongs to carbonate ion is by electrostatic nature, and between two atoms are relatively small electronic density. One of the consequences of energy relations in the crystal is creating the stabile complexes (4) . When we use it like filler, limestone because of such a structure gives special results in dispersion.

Chemistry characteristic of CaCO_3 is that it resolves in the acids what is not favourable influenced on its widest using. The sensibility on acids is decreasing by surface preparing the particles during which we got especially good dispersion in some special system (5). Besides that, by activation the limestone, we got the following effects:

- it gets special hydrophobic characteristic and on that way it decline water and moisture what is very important for every filler
- By the surface preparing it gets the abrasive characteristic CaCO_3
- Such a fillers shows better rheology characteristics, bigger resistance on hit and better electric characteristics
- By using such kind of filler we got more quality surface of the finished product, from the aspect of its smooth, shine and its look.

We need to emphasize that from all the fillers which are using for producing PVC only on fillers type CaCO_3 goes 80% from total spent of fillers (6).

In the first part of this work are given the results of the researches made with the aim of getting coated CaCO_3 from the deposit "Vencac"-Arandjelovac to make better its characteristics and to use like a filler in producing PVC products. In the second part of work are showed the results of the researches got on microscopic way in the aim of fortifying the degree of coating of the researches samples of limestone.

2. Experimental procedure

2.1. Characteristics of the raw material

a) Chemistry composition

Chemistry composition of the sample of the limestone from the deposit "Vencac"-Arandjelovac is showed in table 1.

Table 1. Chemistry composition of the limestone from the deposit "Vencac"-Arandjelovac

Component	CaCO ₃	Fe ₂ O ₃	Al ₂ O ₃	MgO	SiO ₂	CaO	H.L.
Content, %	98.29	0.015	0.038	0.62	0.57	55.07	43.55

Chemistry composition in table 1 shows that the limestone from deposit "Vencac"-Arandjelovac is satisfied quality from the aspect of the content of CaCO₃ and like such it is satisfying the conditions for using like filler.

b) Mineralogy composition

Qualitative mineralogy analysis of the sample of limestone from the deposit Vencac Arandjelovac is made under the polarization microscope for the passed light, by immersion method (immersion xylene) with identification of the present minerals. Amplification of the objective is 3.2-20X.

Mineral composition: calcite, opal, wollastonite, getite-limonite, apathite, rthuite, vesuvianite. Mineral composition is unchanged. Researched sample is total in crystal condition (with exception of opal). The most present mineral is calcite (more then 95 %) while next is opal, then limonite-getite, which appears in the form of film on calcite, or like free, wollastonite and vesuvianite with apathite and rthuite (in traces). Presence of iron minerals (limonite-getite) are in traces.

c) Granulometric composition

Granulometric composition of the researched sample of limestone "Vencac"-Arandjelovac is showed in table 2 and graphically on figure 1.

Table 2. Granulometric composition of limestone "Vencac"- Arandjelovac

Class of grain size, μm	M, %	M% from sieving	M% sieving
+315	0.00	0.00	
-315+208	0.17	0.17	100.00
-208+149	1.11	1.27	99.83
-149+104	5.54	6.81	98.73
-104+74	2.66	9.47	93.19
-74+63	6.86	16.33	90.53
-63+43	3.76	20.09	83.67
-43+37	1.11	21.20	79.91
-37+30	1.18	22.38	78.80
-30+20	5.20	27.58	77.62
-20+15	7.17	34.75	72.42
-15+10	13.79	48.54	65.25
-10+5	27.82	76.36	51.46
-5+0	23.64	100.00	23.64
Σ	100.00		

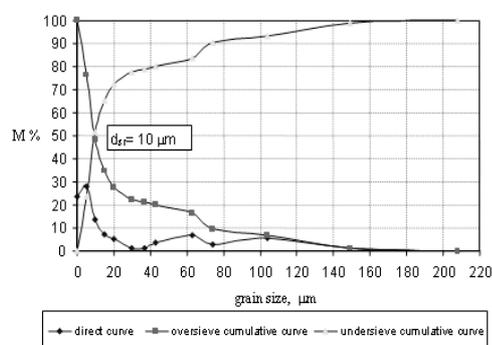


Fig. 1. Diagram of granulometric composition of limestone "Vencac"- Arandjelovac

Other characteristics of the used sample of limestone which are important, too for its using like a filler in PVC products are given in table 3.

Table 3. Characteristics of used sample of limestone

Characteristic of limestone	Result	Standard
Extern look	White dust without mechanic additions	JUS B.B8.080.
Degree of whiteness	93.1% (MgO-100%)	JUS B.B8.084
Adsorption of oil	21.53%	JUS H.C8.202
Content of moisture	0.02% (at 105 °C)	JUS H.C8.202
pH value of the water suspension	9.5	JUS H.C8.209

2.2. Technology procedure of getting the coated limestone

Coating the mineral raw material, apropos fine dust of CaCO_3 from mine "Vencac" Arandjelovac we made on new technology procedure in laboratory conditions with stearic acid. The content of stearic acid in the samples was 1%, 2% and 3%. Coating was made in vibration mill with rings type "KHD HUMBOLDT WEDAG" lasting 7 minutes and previously was warming the mill and mineral raw material on 60 C.

The scheme of the process of coating was showed on the figure 2.

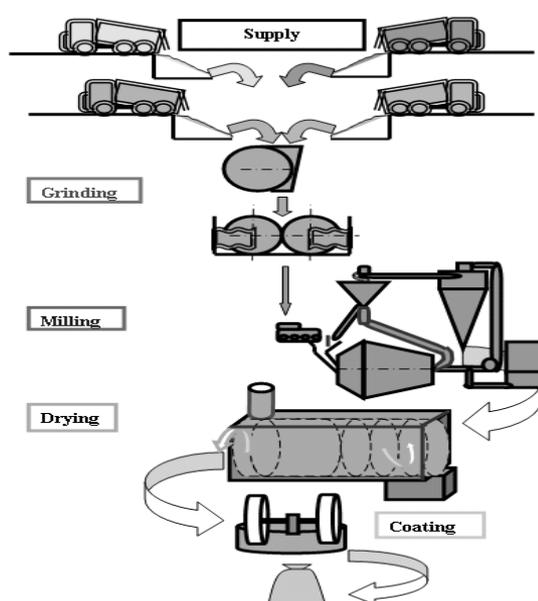


Fig. 2. Scheme of the technology procedure of getting coated limestone

From previous, it could be concluded that with valorization of molybdenum through next few years, RBB income could be raised up to unbelievable 50%. Because of that, this fact must be considered with respect. RTB

2.3. Checking the degree of coating

Checking the degree of coating on the examined samples of limestone is done under the polarisation microscope for the passed light, by immersion method (immersion of waters), in laboratory for mineralogy characterisation ITNMS. Amplification of the objective is 10-50X.

On the figures 3, 4 and 5 are shown the look of examined samples of limestone.

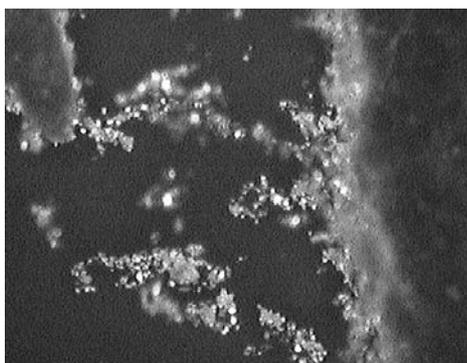


Fig. 3. Look of the coated limestone (content of stearic acid 1%)

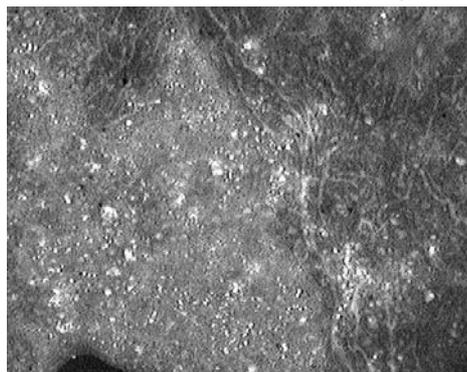


Fig. 4. Look of the coated limestone (content of stearic acid 2%)



Fig. 5. Look of the coated limestone (content of stearic acid 3%)

Results showed that the degree of coating the limestone which is activated with stearic acid whose content in the sample is 1 %, minimum 80 % (Figure 3).

The degree of coating the sample which content 2 % stearic acid is minimum 85 % (figure 4).

The biggest degree of coating (minimum 95 %) is reached in the sample which is activated with stearic acid whose content in the sample is 3 % (Figure 5).

3. Conclusions

Based on results we have got we can conclude following:

- Coating the surface of the particulars of limestone by stearic acid has done successfully in vibration mill with rings.

- Biggest degree of coating was reached in the sample to which is add 3 % stearic acid (min 95 %) while the coating in samples to which was add 1 % and 2 % of stearic acid little lower and approximately similar values (min 80 % and min 85 %)

- During the fortifying the time of lasting the covering we started from the conclusion get into earlier examines that the factor time don't influence on degree of coating.

- Experience data shows that the ideal temperature for coating is 60°C.

On this temperature, stearic acid gets the characteristics of the liquid aggregate condition and like such for the monosediment on the surface of the limestone particular.

4. Acknowledgements

This paper is a result of research relating to the project 006706 that has been funded by the Ministry of Science and Technology of the Republic of Serbia.

5. References

1. Z. Biliskov, A. Jercic, A. Kuzmanic, Calcium carbonate as filler in PVC-products, Proceedings of the First Yugoslav Symposium on nature carbonate fillers for civil engineering and industry, Arandjelovac, (1977), pp. 25-32.
2. N. Bilbija, Nature carbonate fillers, Proceedings of the First Yugoslav Symposium on nature carbonate fillers for civil engineering and industry, Arandjelovac, (1977), pp. 9-14.
3. M. Petrov, Determination of parameters for coating (hydrophobization) of precipitated calcium carbonate (PCC) and nature granulated calcium carbonate (GCC), Internal project, ITNMS, Belgrade, (2000).
4. D. W. Cornwell, Benefits of PCC as a PVC additive, 3rd Minerals in Compounding Conference, Cologne, Germany, (2001), pp.35-37.
5. M. Petrov, Lj. Andric, Z. Sekulic, Thermokinetics of Mineral Powder Coating, 10th European Symposium on Comminution, Heidelberg, Germany. Book of abstracts, B2.5, (2002).
6. M. Petrov, Lj. Andric, S. Milosevic, Lj. Pavlovic, Coating of Mineral Powders by Mechanical Activation, International Conference-Fundamental bases of mechanochemical technologies, Novosibirsk, Russia, (2001), pp. 4-6.