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UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Vienna International Centre, P.O. Box 300, 1400 Vienna, Austria
Tel: (+43-1) 26026-0 · www.unido.org · unido@unido.org

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# GRANULAR PESTICIDES[1]

by

Otto Zeiser
AMONN Fitochimica S.p.A.
Bolzano Italy

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# CONTENTS

## Introduction

Granules are becoming of great importance in industry,agriculture and other areas of our life. Granules may be used to improve storage and transport stabilty,to provide simpler use and better results.This holds true for instant milk powder, fertilizers and encapsulated seeds.

Granulated pesticides have gained greater importance only in the last years.Even though practically every pesticide can be formulated as granules, their use remained limited.There may be various reasons for this:higher price,lack of equipment or availability and wide use of persistent pesticides. Recently,granulated pesticides are used more and more extensively.We have good reasons to welcome this.We can more efficiently resolve many problems with the aid of granulated pesticides.In this paper I will present four aspects:

-general characteristics

-formulation processes

-application

-residues and toxicity hazards.

Granules are mixtures of active compound and inert matter.Their particle size range between hundred and several thousand microns.In many cases,surfactants are absent.Stabilisers and binders are common adjuvants.

There is no standard operation for producing granules.
Some active material may need a particular carrier composition to combine mechanical and chemical stability with good field performance.
Often granular pesticides are difficult to formulate and need much effort and time before being marketable.
Sometimes there is no problem at all.
The best known formulation method is

- Impregnation, a simple operation with large output and low investment.

Other methods can be:

- Agglomeration, used to form bentonite inert granules, first step in tablet forming and compaction.
- Compaction may become of greater importance in the future, but needs heavy investment.

Extrusion is often used, but is feasible for few compounds only.

I shall also mention new processes

- Microencapsulation. In the USA microencapsulated methylparathion is field tested on a large scale this summer.
- Microgranules will find a limited application.

General Characteristics

Various characteristics of granular pesticides should be determined:specific gravity or bulk density,also number of particles per gram,water content,moisture uptake,swelling with water,abrasion and dust formation.

The most obvious characteristic is particle size, defined by dry sieve analysis with standard sieves. Granular formulations have a characteristic particle size distribution.The narrower particle range, the better uniform coverage.

Dust content must be minimized in granules because of drift,toxicity hazards and danger of overdosage. Dust may be defined by a particle size smaller than 40 microns.USDA allow no more than 5%fines smaller than 250 microns.

Recently microgranules with particles between 100 and 200 microns were proposed under appropriate conditions.Microgranules should not contain particles below 40 microns.

Microencapsulated liquids may be as fine as 10 microns.

TABLE 1 (see page 22)

There is a significant difference between pesticidal dust,microgranules,granules and macrogranules when the same active material is applied at the same dose per surface area.

In most cases the various formulations have in common that they act by vaporisation,aqueous solution or both.
Usually no surface active compounds are incorporated in pesticide granules.In effct,this distincts them from wettable,in water dispersable,powders.
Granules can be spherical,but they are mostly non-spherical shaped.
Distribution of active material within or on the granules may be homogeneous or heterogeneous, depending on the formulation process.
Compaction of mixed powders gives evenly distributed active compounds.
Impregnation of sorptive carriers with liquid or liquidised pesticides occurs less evenly.In this case the sorptive carrier can have a high inner surface.This inner surface is given by porosity and diameter of micropores.This inner surface is independent of particle size.

TABLE 2 (see page 23)

On nonsorptive granules such as fertilizers, reasonable amounts of pesticide can be deposited with binders.This deposit is sometimes easily sheared off by abrasion and gives dust of high active material contents.
Coating with oily layers,films of plastics or pigments is therefore fairly often exercised; if necessary in combination with natural or synthetic gums.Such layers encapsulate or rather

cover granules,giving them more mechanical stabilty for transport and graded release after application.

In some cases we may want to regulate the desintergration of the granules soon after application. This can be achieved with swelling carriers,such as bentonite.When moistened by rain or in contact with wet soil,especially if some wetting agent is present,swelling bentonite desintegrate pesticide granules.

New techniques are still invented,they have not yet exhausted all possibilties to control the characteristics of granules.

To obtain a good product the formulator has to consider the chemical and physical properties of the active material,first:solubilty in water,stability to hydrolysis,volatility, compatibility with carrier,adsorption and decomposition in soil and the like.

Close cooporation with the agronomist is advisable.Environment and climate can significantly affect the performance in regard to crop and pests.

Intensive field trials give indications about the active material to be used.Quality and quantities should be based on practical results.

Formulation processes

If the formula is elaborated ,greater quantities have to be produced.It is not always easy to obtain stable granules economically.

Economic factors to be considered are:costs and availability of inert material,quantities to be produced within a given period and quantities to be produced in the next years.This decides capacity and degree of automation of the installation,and capital spending.Personel has to be trained.The maintenance goup must be equiped.Production costs have to be calculated.

Now a short description of the formulation processes

1 Impregnation

Impregnation is absorptio of liquid or liquidized pesticides in preformed,sorptive granules.Sorptivity of the carrier gives the percentage of liquid matter that can be absorbed.

If the pesticide is a solid,it can be dissolved in nonvolatil solvents.Dispersions of finely ground pesticides can also be sprayed on inert granules.

In most cases impregnation leads to good results. This method should therefore always be considered first.

The properties and performance of impregnated granules depends on the inert carrier:

Organic carriers:wood flour,ground tobacco stems,
corn cobs,coffee grounds,walnut shell flour and other sorptives.Waste of synthetic matter can also be used.

Inorganic carriers:granular clays,especially of the montmorillonite group is often used. Bentonite,attapulgite and sepiolite are well known.

Pumice is highly sorptive,but also abrasive.

Calcined diatomite may be usefull.

Granulated fertilizermay be a carrier.

The choice of a good carrier is often difficult. Pesticides can be decomposed by the carrier,particularly by clays.On the large inner surface are active sites. Pesticides may be adsorbed and decomposed catalytically. Spontaneous decomposition is possible and can lead to ignition.

It is possible to inactivate these sites with urea, hexa or glycols and the like.Granules are impregnated with 5-10% deactivator prior to impregnation.Talloil may be applied as stabiliser with the active compound. Deactivation is not always necessary,but it deserves attention.

Studies on compatibility of carrier and pesticide is a must.This can be done by formulating the product with well defined concentrations.The granules are stored at elevated temperatures during a given time.At intervals the product is analysed chemically.The original content has to be checked.

If no significant decomposition after a few month at 50°C is noticeable, the formulation can be considered stable.

A better indication, however, should be given by storage under the conditions in practice and there may be unpleasent surprises. Finally it is the performance in the field test, that gives the answer.

The impregnation process itselfe is no great problem. In the laboratory every type of rotary blender equiped with an injector for the liquid gives already indicative results.

Results representative with respect to dust formation can be obtained only by using mixers of at least 200 l capacity.

Dust formation can be a problem

TABLE 3 (see page 24)

Untreated bentonite granules may have a favorable particle size distribution. If theirstability is not good or treatment is to rude, impregnated granules contain to much fines.

Active material is sprayed at a pressure of 3-5 atm with full cone nozzles. This may be done by pumping with a gear pump or with air pressure out of a pressure vessel.

With a concrete mixer of 3-5 $m^3$ one can obtain good results up to 2 ton/batch operation. But any other rotating drum, tumbler or not, is good for impregnation, if injection of the liquid compound is possible.

A flow sheet is given in

TABLE 4 (see page 25)

If inert granules are transported with a screw conveyor at a constant rate,continuous impregnation is possible.The liquid is injected into the bypassing granules.This installation can be fully automised.
Now I shall present a cost calculation.

TABLE 5 (see page 26)

This is to confront a batch operation with 500 tons per year output with a semiautomatic and a fully automised installation.
I had to make assumptions based on my own experience.
Manhours are calculated with 3$/hour.Amortisation is made in 10 years.Capital costs are calculated with 5% over this period.Direct and indirect costs may be different.
I will show that simple and appropriate installations gives the best results and not high sophisticated equipment.
Most important is capacity.Each installation has a optimum capacity.It is always a problem to determine and to reach this optimum.No installation can be used with full load all over the year.
Operation costs for granules in a well balanced installation are not greater than costs for a wettable powder formulation.
But whereas inerts for wettable powders cost 10-40$/ton, the inert carrier for granules costs 40-80$/ton.
Organic carriers may make it possible to reduce material

costs.Higher material costs are balanced by lower application costs,as I will show later.

2 Agglomeration

Agglomeration of finely divided and well mixed powders is effected by rotation and simultaneously moistening the powder with 5-25% water.The percentage of water depends on material and blender characteristi The amount of water,time,temperature,the speed of revolutions and shape of paddles is critical.
A well known agglomeration process is pelletising, used for fertilizers,baits and inert bentonite granules

Table 6 (see page 27)

Granules must be dried,sifted,crushed and again sifted.Fines must be recycled.
Pesticide granules need binders.A few percent of ligninsulphonate may suffice to minimise dusting.
In this process water has to be evaporated at elevated temperatures.This may cause decomposition of active material.Operation costs are effected considerable.
In this connection I have to mention the Diamond-Alcali process.Granules are being formed by using mixtures of gypsum and ammonium - or aluminiumsulphat as a carrier composition.In the presence of 5-30% pesticide the mixture is rotated and wetted to agglomerate granules.

Gypsum and ammoniumsulphate in the presence of water give stable adducts, containing chemically bound water. So granules can be dried at low temperatures.

3 Compaction

Compaction is accomplished by passing a moist mixture of powders through steel rolls. The powder is compacted under enormous pressures, whereby temperatures of 80°C and more are reached. Thus evaporates the greatest part of water.

With fertilisers and with matter of some plasticity rather dense granules can be obtained after desintegrating the compacted sheets.

For pesticides binders are needed.

Care must be taken, that the powder to be compacted does not contain excessive amounts of air. The powder must be deaerated before compaction. This can be a problem. Controlled desintegration of the compacted sheets followed by sifting out the needed fractions gives 80% fairly firm, irregularly shaped granules. They may be coated afterwards, to stand better abrasion during transport and handling.

TABLE 7 (see page 28)

This procedure lends itself to controlled release, because different effects can be build in.

The process as such is complex and needs high investment of capital. The process is feasible with an output of 10.000 tons/year.

4 Extrusion

Extrusion is performed by pressing a pasty mass through small openings. Also oscillating rolls can pass over a sieve thus extrudingthe material. A rotating knife cuts the threads in small pieces. 5%metaldehyd with organic fillers give macrogranules for baits without drying. Unfortunatly enough all other formulations need an expensive drying process. Carriers as bentonite form thixotropic masses, but they need great quantities of water. 20% and more water has to be used and evaporated. Dolomite as carrier would need only 5% water. This fact illustrates the importance of properly selected carriers.

Extrusion is in Japan a common process, may be because paddies need very stable granules, may be, because bentonite is available and energy is cheap. This process is only possible with stable, nonvolatile pesticides.

5 Microencapsulation

Microencapsulation of liquids to form granules with all characteristics of dry matter is a most important process. Pesticides are not yet encapsulated on a large scale

TABLES 8,9 (see pages 29 and 30)

Encapsulation may be achieved by

- phase separation by coacervation
- interfacial reactions by polymerisation of monomers
- physical methods as spray coating in a fluidised bed

Pennwalt encapsulates methylparathion. Particle size will be 10-40 microns. Formulation is made as wettable powder. There will be no problem, to make coarser granular formulations . Important is, that release can be controlled. In the first experimental formulations microencapsulation is timed for three weeks.
Mirex is encapsulated by NCR as baits for fire ants .
Pennwalt is encapsulating disparlure, the isolated sex attractant of the gypsy moth.
Formulation costs for this process are very high and at the moment are only a few companies spezialised in this technique.

6 Microgranules

Microgranules were developed by a german formulator to applicate herbicides of the hormon group with lesser costs and reduced drift. Microgranules are highly concentrated granules with application rates of 5-10 kg/ha. Formulation and application may give problems.

Application

The application of granules is cheaper and simpler than conventional spraying.Taking into account manpower,machinery and maintenance,10$/ha are needed for conventional spray treatment.The same treatment with granules costs only half this amount, i.e.5$/ha.The higher price of granular formulation can be compensated by lower treatment costs.
But even if it is not possible to compensate the higher price(comparisons of this kind are always dubious)we have strong arguments for using granules. A few of them are:simple application,in some cases without any machinery at all;no problem with the preparation of dispersions or emulsions;no use of water,no pumping and nozzle problems;no drift of highly toxic material,less danger for farmers.
Application of granules gives possibilities for better results.With one treatment of aldicarb granules aphids on roses are controlled at least for 6 weeks. Submerged weeds are controlled with dichlobenil or diuron granules,no other formulation is effective.
To achieve pest and weed control,1-10 kg/ha of well choosen material has to be deposited in predetermined locations.This may be a spot,a row of plants or the entire field for a homogeneous overall treatment.
Spot treatments are made with a tube equipped with a simple dosage device or by hand.

Band treatments may be made with drill machines or with one of several devices in use.They have up to 6 meter total length.

The best application machinery works by pneumatic distribution.An air blow carries a continuous jet of particles to bands of 20-200 cm width.

These pneumatic distributers are also good for overall treatments.

Overall treatment can also be made with fertiliser distributers if they are calibrated exactly.The problem in this case is exactness:fertilisers are used with 1000 kg/ha and more.It is not critical if some rows are t reated twice.Herbicides are applied with 50-100 kg/ha.An overdose may mean a heavy loss or complete kill of the crop.

Drift is no problem with conventional granules

TABLE 10 (see page 31)

demonstrates drift measured for dichlobenil granules at various wind velocities.With microgranules drift is a problem and there should be no wind during application.

Granules can be easily mixed with other granules if they have the same cornsize range and the same specific gravity.Otherwise there may be problems with separation.

The distribution pattern is characteristic for only one spesific granule.Calibration should be made for every new formulation.

Application of granules may be in soil,on plants or in water.

Application in soil

Application in soil involves a combination of different factors:type of soil,structure,nutrient status micro-organism,water content,temperature and many others.

Fumigants are not easy to use.Granulated Nemagon is easy to use.Granulated Dazomet releases the toxic gaseous phase of methylisothiocyanate slower.Application is easer,because there is no drift of dust.

Nematocides are often highly toxic compounds.

Granules gives less toxic hazards.Aldicarb absorbed on an organic carrier,coated and containing a warning odor gives excellent results and is easy to applicate.

Soil insects as wire worms,gross grubs,rootworms and cutworms are well controlled with aldringranules. The carrier may be a fertiliser.Residues with aldrin are becoming a problem.Not so persistent insecticides have to be used.The problem is,that these compounds are decomposed by hydrolysis or by biodegradation, before they can act.

Granulation controls release,but does not change the nature of a principle.Degradation depends on temperature,acidity,movement aeration,rate of application and amount of water.

Decomposition in soil was studied by many authors. P.T.Walker gives a good survey in volume 40 of residue reviews.

Parathion,applied with 5 kg/ha may be decomposed to 70 % after 12 days(E.P.Lichtenstein J.Econ.Entom. 57,618-627(1964).In mediteranean climate this may be 6 weeks.Depending on insect species considered and time of application,this period may be enough to give sufficent control from 10 weeks to a full season. There is a number of phosphorous compounds with persistens up to 6 month:fensulfothion, trichloronate,chlorfenvinfor But these compounds have a higher price.So is it interesting to formulate and applicate parathion granules carefully,with confrontable results.

Fungicides as quintozene can be phytotoxic to some crops. Granulation with controlled release resolves this problem

On Plants.

On plants granules give possibilities for selective effects.In cereals broadleafed weeds are treated with 2,4-D,MCPA and similar compounds.With conventional spray techniques drift is a problem,especially if vineyards are nearby.Microgranules applied with 5-10 kg/ha adhere on broadleafed weeds better than on cereals and grasses.Drift is not so great as with conventional sprays.

Conventional granules would not adhere,thus falling onto the soil.The pesticide penetrate through the upper soil layer and finally reach the rootsystems.

Results may be quite different as compared with microgranules of the same pesticide.

Cornborer control is possible with carbarylgranules, because granules mainly fall and collect in the leaf sheath of developing corn, right there remains the borer. With rain or dew small amounts of carbaryl are desolved, sufficent to control the cornborer.

In water

Controling pests in water is often a problem if they live on the bottom of canals, lakes, paddies. With granules it is possible to reach them.

Developing submerged weed may be controlled with herbicides as dichlobenil. For example a canal of 10 m width is treated with two applicators on the embankements. It is possible to treat 3-5 km/hour. The same results may be obtained with treatments from a boat.

The highest concentration of pesticide in water is given by its solubility. Pesticides with high water solubility must be carefully applied.

Since pesticides are absorbed by plants and plankton, accumulation in fish is possible, even if the solubilty in water is not high.

Residue problems and toxicological hazards are connected with the various characteristics of the particular pesticide and it is not only a matter of its intrinsic toxicity.

By formulating hazardous pesticides in a granular form it is to a limited extent possible to keep its unwanted side effects somewhat under control.But one cannot possibly expect to eliminate hasards completely.

Theoretically,a compound that would decompose easily can be encapsulated so,that it will always remain within the wall and thus never become active.

In praxis there are factors that bring about changes at the surface of the capsules.Humidity, temperature and microorganisms are such factors. The encapsulated compound will not always be released to the same extent and with the same speed. Only the reasonable use of the various experiences may lead to further progress.

We are entering into a period of increasing spesialisation more sophisticated methods,complicated compounds and many problems are yet to be solved.

I tried to present you in a short time with important facts about characteristics,formulation processes and application possibilities of granular pesticides.

## PARTICLE SIZE CHARACTERISTICS

| | AVERAGE PARTICLE SIZE IN MICRON | ALLOWED MAXIMUM DEVIATION |
|---|---|---|
| DUST | $< 45$ | MAX 5% $> 45$ MICRON |
| MICROGRANULES | 100 - 200 | NO DUST |
| GRANULES | 250 - 2000 | MAX 5% $< 250$ MICRON |
| MACROGRANULES | $> 2000$ | NO DUST |

**TABLE 1**

SORPTIVE CAPACITY

| | BULK DENSITY $g/cm^3$ | AMOUNT OF WATER TAKEN WP TO THE WET FLOW POINT $cm^3/g$ | SPEZIFIC SURFACE (WATER SORPTION TECHNIQUE) $m^2/g$ |
|---|---|---|---|
| TALC | 0.4 - 0.6 | 1.00 - 1.28 | 1.8 - 15.8 |
| MICA | 0.5 | 1.10 | 2.6 |
| BOTANICALS | 0.2 - 0.4 | 1.70 - 4.52 | - |
| MONTMORILLONOID GROUP | 0.4 - 0.6 | 1.40 - 1.85* <br> 8.00 - 8.53** | 294 - 391 |
| ATTAPULGIT | 0.3 - 0.5 | - | 120 - 140 |
| SYNTHETIC $SiO_2$ | 0.20 - 0.25 | 2.55 | 210 |

* NO SWELLING

** SWELLING

SOURCE: HANDBOOK OF INSECTICIDE CARRIERS

TABLE 2

## PARTICLE SIZE DISTRIBUTION OF BENTONITE GRANULES

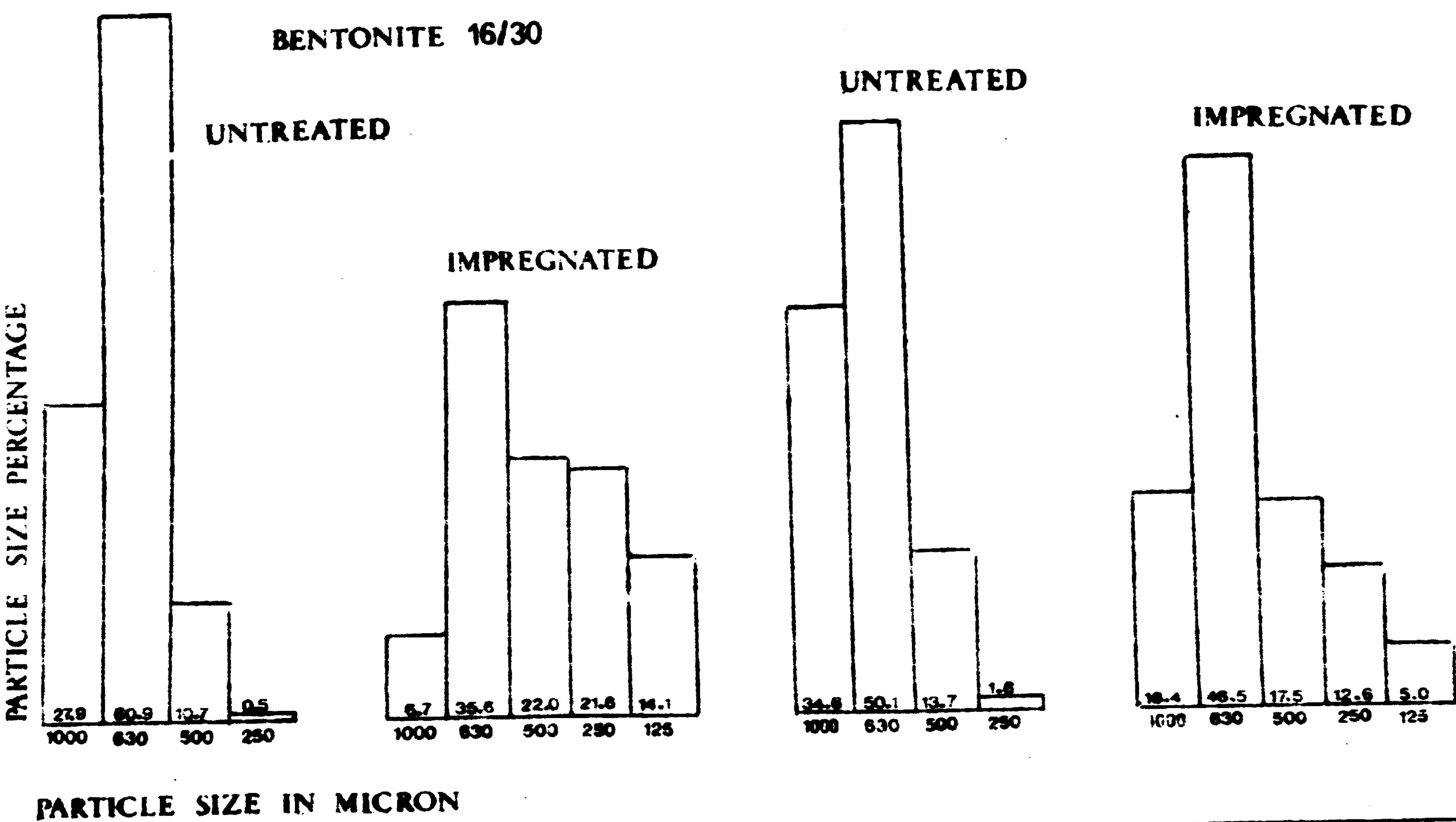



TABLE 3

IMPREGNATION OF GRANULES

FLOW SHEET

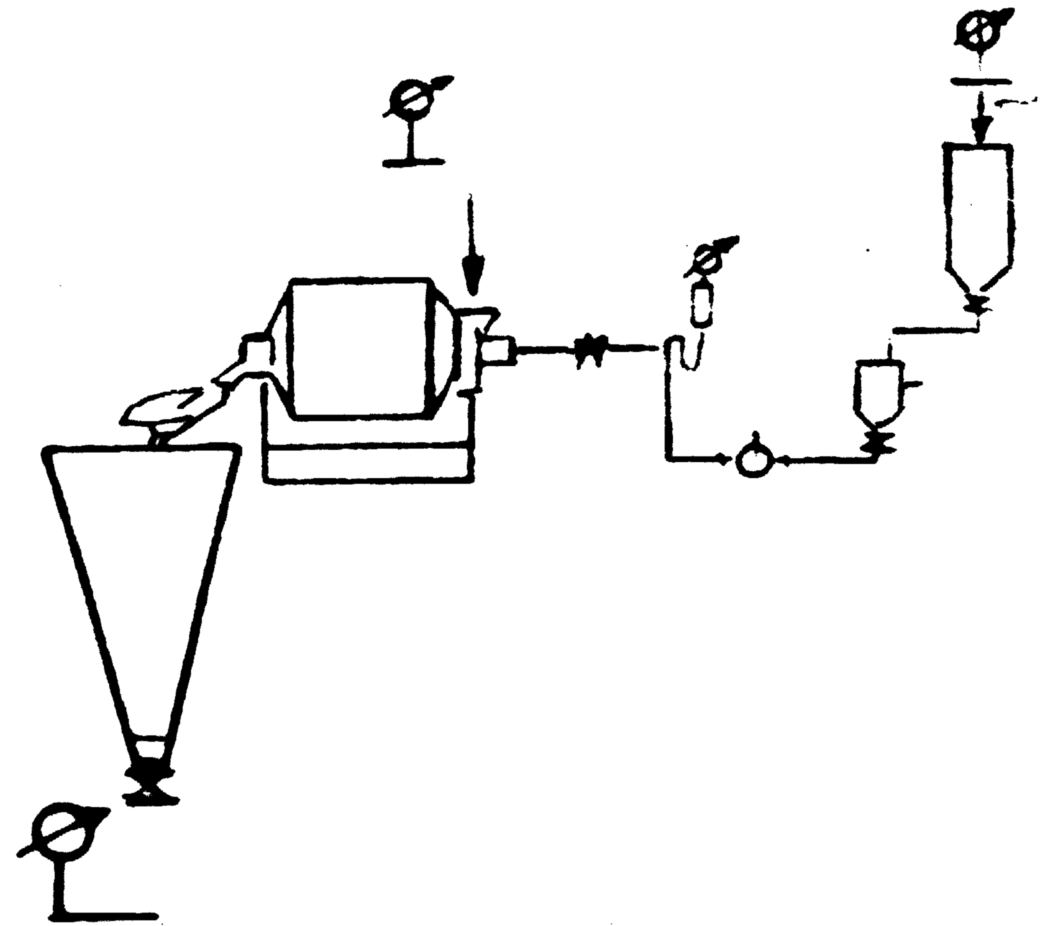


TABLE 4

## COST CALCULATION FOR IMPREGNATION

| | BATCH | SEMIAUTOMATIC | AUTOMATIC | |
|---|---|---|---|---|
| CAPITAL INVESTED | 30.000 $ | 50.000 $ | 200.000 $ | |
| DAILY OUTPUT | 5 tons | 8 tons | 40 tons | |
| No. OF WORKERS | 8 | 4 | 7 | |
| VG FINISHED PRODUCT PER WORKINGHOUR | 80 | 300 | 750 | |
| YEARLY OUTPUT MAX. | 500 | 1.000 | 10.000 | |
| YEARLY OUTPUT EFF. | 500 | 500 | 500 | 3.000 |
| OPERATION COST PER TON | | | | |
| | 3.000/500 | 5.000/500 | 20.000/500 | 20.000/3.000 |
| AMORTISATION 10 YEARS WITHIN | 6.0 | 10.0 | 40.0 | 6.7 |
| INTEREST 5% OF INVESTED CAPITAL | 3.0 | 5.0 | 20.0 | 3.3 |
| DIRECT WAGES | 37.0 | 10.0 | 4.0 | 4.0 |
| DIRECT COSTS | 3.0 | 10.0 | 20.0 | 20.0 |
| INDIRECT COSTS | 5.0 | 5.0 | 5.0 | 5.0 |
| TOTAL PER TON | 54.0 | 40.0 | 89.0 | 39.0 |

TABLE 5

## AGGLOMERATION FLOW SHEET

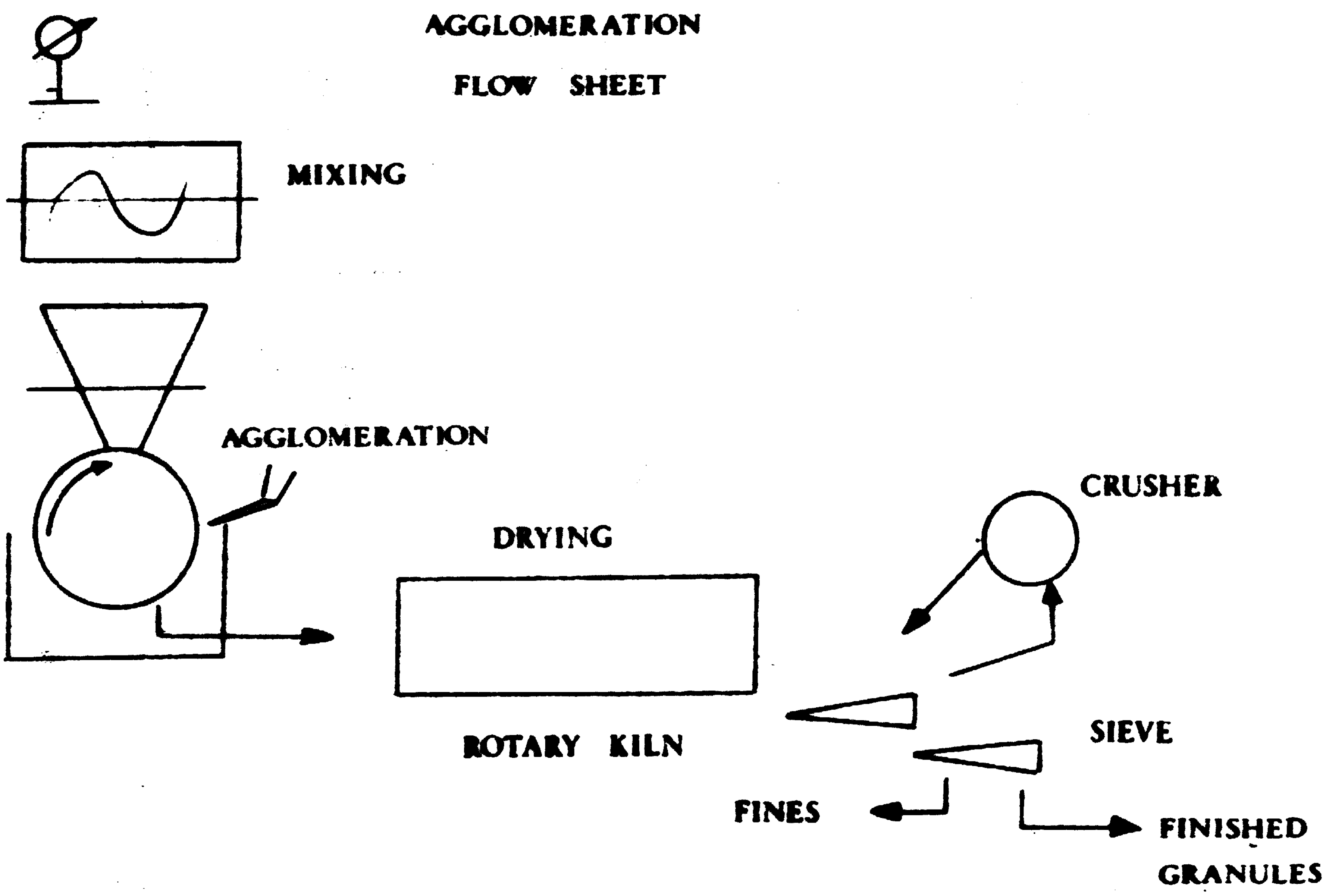



TABLE 6

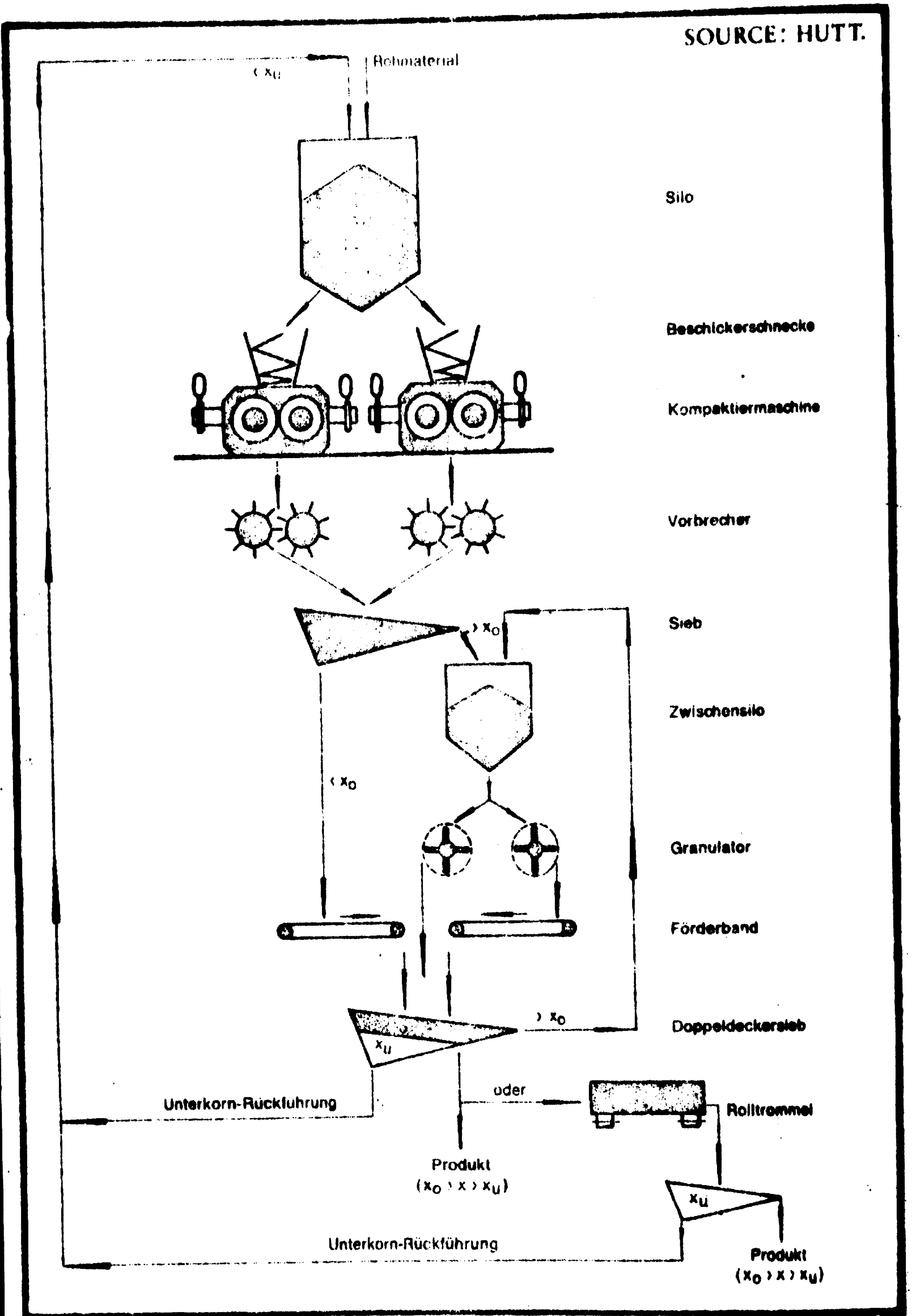
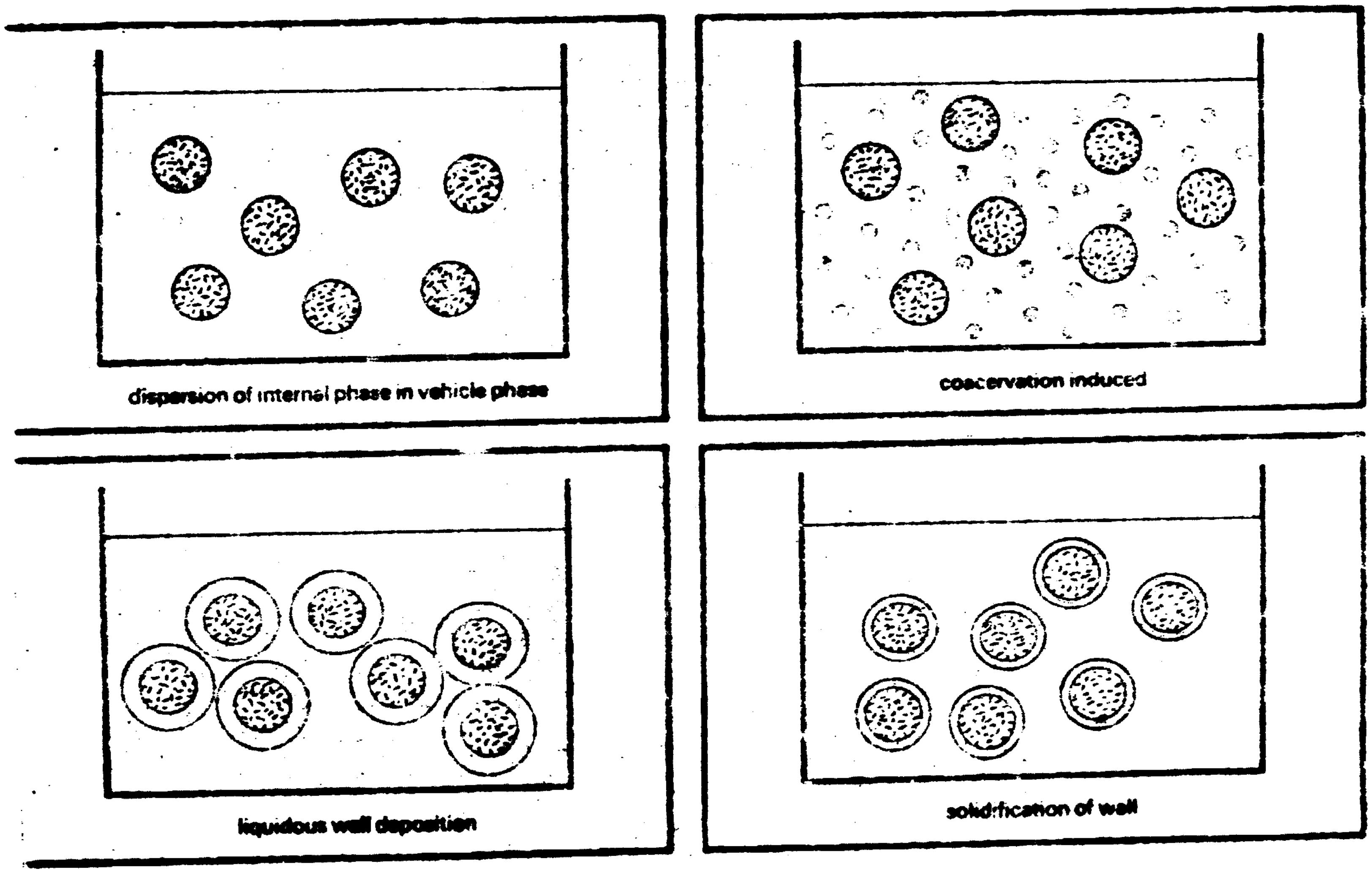

SOURCE: HUTT.
< xu
Rohmaterial
Silo
Beschickerschnecke
Kompaktiermaschine
Vorbrecher
Sieb
> xo
Zwischensilo
< xo
Granulator
Förderband
> xo
Doppeldeckersieb
xu
oder
Rolltrommel
Unterkorn-Rückfuhrung
Produkt
(xo > x > xu)
xu
Unterkorn-Rückführung
Produkt
(xo > x > xu)

TABLE 7

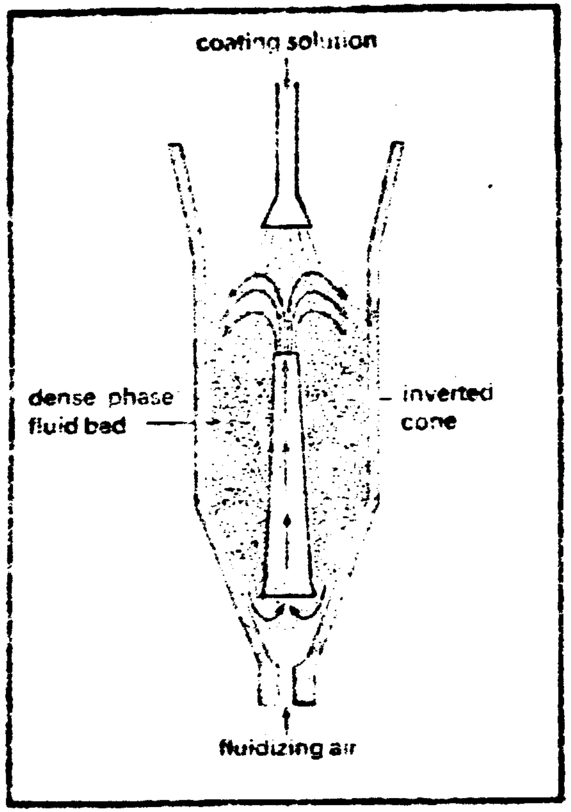
# MICROENCAPSULATION B4 COACERVATION

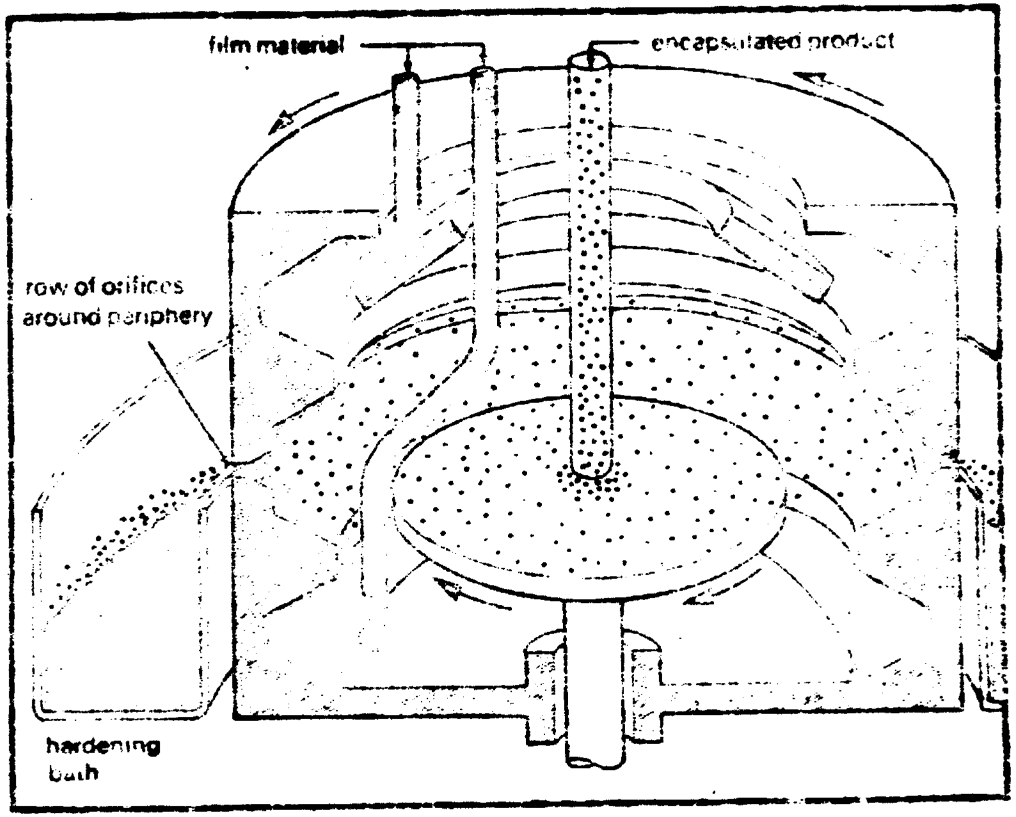



OACERVATION is the method most commonly used to form microcapsules. Initially the core material to be encapsulated (the internal phase, depicted as grey spheres) exists as a dispersion suspended in a liquid (the vehicle phase, in pale colour) in which it must be immiscible. A wall material, such as gelatin, is also suspended as a sol in the dispersion medium or actually dissolved in it (this, the external phase, is therefore not visually evident in the first illustration). To induce coacervation the temperature, pH or composition of the system is changed in some significant and carefully controlled way. The wall material comes out of solution (as the coacervate, shown in deep colour) and eventually aggregates around the core particles to form continuous encapsulating walls. These are then hardened

TABLE 8

# MICROENCAPSULATION WITH MECHANICAL METHODS




**MECHANICAL METHODS** of encapsulation are preferred for some systems and research into these techniques is very active. In the modified fluidized bed method (left) air is pumped vertically up through a dense fluid bed of core particles. The latter, which may be either solid or liquid, constantly circulate and are blown upwards at high speed through a tapering cone. Wall material is deposited on the relatively widely separated particles above this cone. Centrifugal encapsulation follows a principle patented by the US Southwest Research Institute (right). Wall material is fed to the inside of a spinning drum and escapes through fine peripheral holes. Core particles are flung from a rotating disc and build up on the wall membrane over each escape hole. When enough core has gathered at one hole centrifugal force causes it to distend the wall membrane through the hole and tear it away to form a microcapsule, which then drops into the hardening bath. The hole is immediately re-covered by fresh wall membrane and the process continues.

TABLE 9

## DRIFT OF DICHLOBENILGRANULES AT VARIOUS WIND VELOCITIES

| WIND IN METERS / SEC. | 0.5 | | | 12 | | | 2 | | | 5 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| FALL HEIGHT IN CM | 20 | 40 | 60 | 20 | 40 | 60 | 20 | 40 | 60 | 20 | 40 | 60 |
| GRANULES 0,25 - 0,5 MM | 1,5 | 15 | 4 | 2 | 2 | 8,5 | 4 | 8 | 16 | 8,5 | 29 | 50 |
| SIZE 0,5 - 1 MM | 1 | 1,5 | 3 | 1,5 | 1,5 | 4 | 3 | 4,5 | 9 | 6 | 15 | 30 |

drift in cm

TABLE 10

30. 11. 73