# Ecological Oil Bonding Agent

- Based on Leaves –

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# 1. Basics

## 1.1 Definition: Oil Bonding Agent

An Oil Bonding Agent is a material used to soarmk up leaked oil, for example after a car accident. There are certain requirements formulated by the ministry of the environment [1] an oil bonding agent should have:
- It mustn't contain any harmful ingredients
- It mustn't change the chemical, physical or biological quality of the water and the ground in a bad way
- It mustn't decompose or inflame when stored in a usual way
- It mustn't contain any clumps or foreign materials

## 1.2 Hydrocarbons - A Threat to the Environment

Hydrocarbons are materials like gas, oil or diesel. Those are all made out of carbon-hydrogen compounds. Some of them are a threat to the environment because once leaked on water they form a thin film on it's surface and therefor make it brackish. Only one drop is able to contaminate up to 600l of drinking water.
On top of that, some fuels contain condiments like benzene that even have mutagenic qualities.

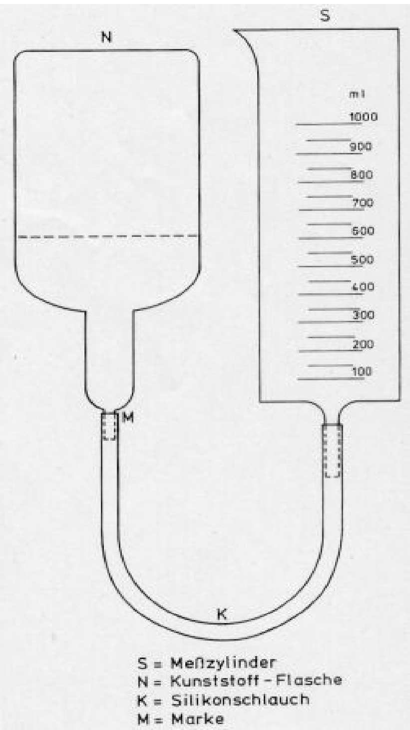
This picture shows some firemen who try to remove leaked oil from a road. A car must have lost fuel during the ride. Such incidents occur every now and then. That'y why a good oil bonding agent is indispensable.

Four years ago we decided to participate in a local competition and therefor looked for a appropriate project. We decided to focus on the leaves which fall down on the street every year. What happens to that foliage? We did some research and found out that it only lies there a couple of days. Then the building yard has the duty to collect and to composte it. Biological material can usually be used for biogas stations. But it isnt't allowed to do so with leaves because some them contain tanning agents that would influence that process and so it has to be composted very expensive. Every tonne of foliage costs the building yard about 160€ and is not even dependend on the emerged garden mould. We decided to change that and used the foliage's attribute to soak up water to develop a strong oil bonding agent based on leaves.

# 2. First Steps

## 2.1 Foliage as an Oil Bonding Agent

First we had to check if pure was able to absorb oil in laboratory conditions. So we needed a gadget to find out the bonding ability of leaves. We found out that the "Gemeinsames Ministerialblatt Nr. 18" has already defined a unified gadget and experiment in order to find that out. We took a description based on that document:



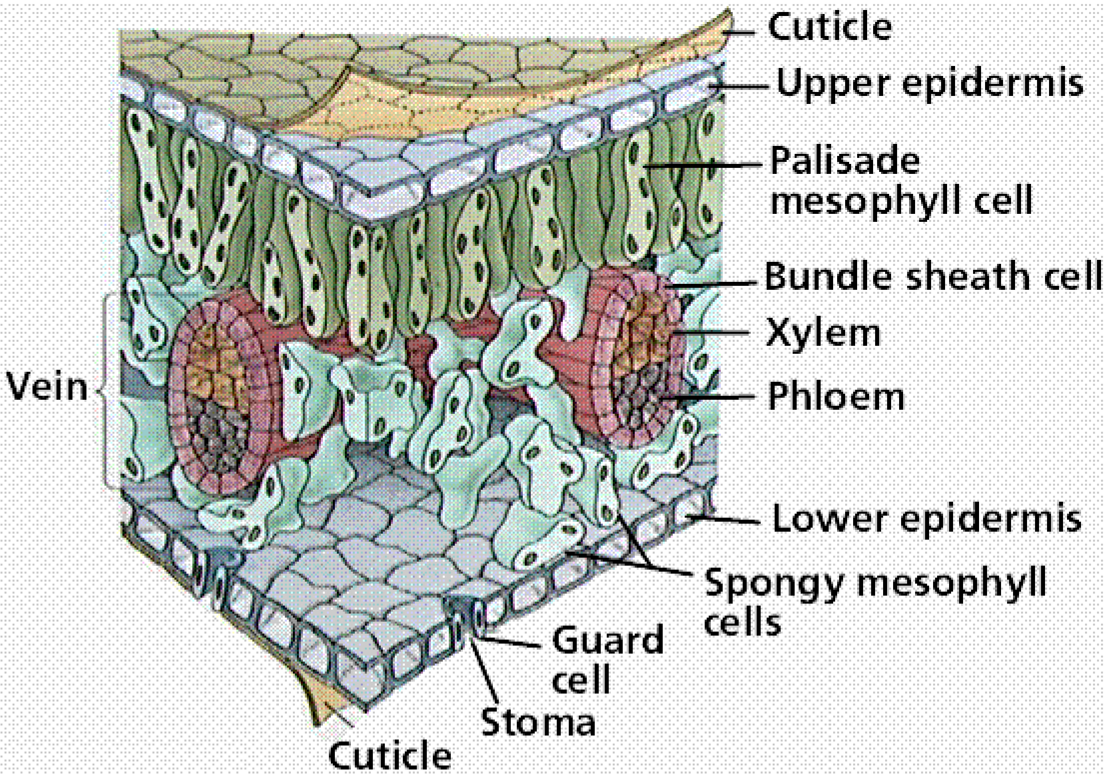

We replaced the plastic bottle N with a funnel in which we stretched a reticule on which we placed the foliage. Instead of the graduated cylinder S we used a dropping funnel.

The test material is placed on the reticule. Then we lead paraffin oil from the dropping funnel through the silicon hose K to the reticule. There it has to stay exact one hour. Then we lead it back to the dropping funnel and so are able to check how much oil has stayed in the bonding agent.

With this gadget we did all our experiments. We started with pure, dry leaves to check if it was capable at all.
So we tested different local sorts of foliage, like maple, lime, walnut and hazelnut concerning their bonding ability. We found out, that there were diffences in their capability: While lime and maple bond about 7 and 6 ml per gramm, hazel and walnut only bond 4ml/g.
Besides those single experiments we also tested a mixture of all of them and got 6ml/g. It would be unefficient to divide the single sorts up and so only the mixture value is relevant. Still we made all our further experiments only with lime leaves for a better basis of comparison.
All values mentioned in our text are averages from at least five experiments. This provides a very high accuracy.
With our first experiments we not only proved that foliage is able to soak up oil but also that it's bonding ability differs from sort to sort. That leads us to the conclusion that there must be a specific foliage characteristic that is responsible for it's efficiency.

## 2.2 Theory of Oil Absorbtion

Using a schematic leaf cross-section we assumed that there might be a connection between size and quantity of the stoma and the cavities behind them.

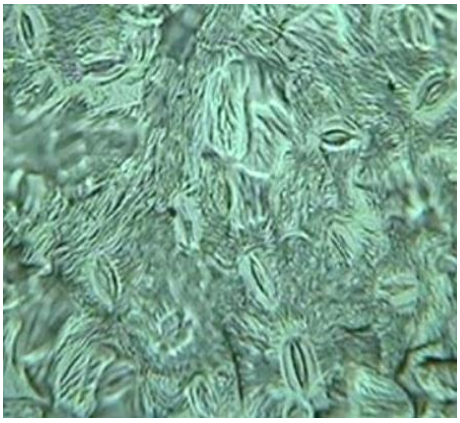


At the bottom side of every leaf, each cm² there are 50-500 Stoma. Behind them, there are the leaf cavities that are important for the gas exchange of the plant. They are small enough to stay intact even when the leaf is hackled.

Picture of a stoma [2]:


Scanning electron microscope (SEM) picture of a the bottom side of a melissa leaf (2000 times enlargement).
When the leaf is dead and dried up, the stoma is still opened (right picture).

That means, that if our theory is right, we should be able to see a difference concerning the size and quantity of the stoma of the different sorts of the foliage, we have already tested. So we took a light optical microscope and tried to find out, if we were right:



The left picture shows the bottom side of a lime (good quality), the right one the bottom side of a walnut leaf (bad quality).

A difference focussed on the stoma is evident. The lime's are more open and therefore better for the oil's entrance. This would fit with our theory.

## 2.3 Modification needed

Pure foliage is unsuitable as an oil bonding agent because of two reasons:
1. Unmodified leaves have a natural barrier against the intrusion of water. Some use micro hairs (surface tension of the water) others a thin film of wax to keep the water outside. Once seperated from its plant, that protection won't be regenerated at all. That means, that if it once got wet, the leaf loses its barrier and soaks up water, too. An oil bonding agent mustn't absorb water because, if he does, it's bonding ability would be harmed if used on water. Many accidents where oil bonding agents are needed occur during rain or even on sea.

2. The apparent density (mass per capacity) of pure foliage is too low. It would be blown away by the wind.

So we needed to find at least one additive that would solve these problems. To keep up our biological attribute, this additive needed to be environment-friendly and bio-degradable, too.
We startet with normal materials everybody has at home, like flour, glue or gelatine but weren't content with the result. We've also tested some tensides but again: we weren't pleased.
So we needed to do some research again. We looked for an additive, that was on the one hand hydrophilic but on the other keeps the water away. We found our additive in methyl cellulose, a bonding agent that is used in many different branches. Methyl cellulose is a highly viscous cellulose ether that finds practice in glue production and even in ice cream.
This additive solved both of our problems but was quite expensive. For our laboratory experiments, we didn't have to care about that.

## 2.4 Recipe

After we have found our additive, we needed to find the right mixing ratio. We tested pure methyl cellulose for its bonding ability and found out, that it was nearly equal to zero. That meant, that we have to keep the part of the additive little enough, so that it won't influence the bonding ability of pure foliage.

We present our results in the following table (MC = Methyl Cellulose):

| MASS RATIO | MASS | VOLUME OF ABSORBED OIL | PER GRAMM BONDING AGENT |
|---|---|---|---|
| 1:1 Lime – MC | 10g | 40ml | 4ml |
| 2:1 Lime – MC | 10g | 50ml | 5ml |
| 5:1 Lime – MC | 10g | 65ml | 6,5ml |
| 7:1 Lime – MC | 10g | 70ml | 7ml |

These results lead us to the assurance that it was possible to create an environment friendly and bio-degenerable oil bonding agent based on foliage. The main idea, to do something useful with leaves was fulfilled. Now we decided to make our product less expensive and suitable for the free market. Now we focussed on practice relevence, manufacturing technics and our competatives.

## 3. Further Development

### 3.1 Adaptation into Practice

After having finished the theoretical part of our project, we decided to test some more plants, that grow mainly in the cities. We also started to cooperate with our local building yard. They gave us a sample of different leaves directly from a road sweeper used the day before. We came to a remarkable result (lime as basis of comparison):

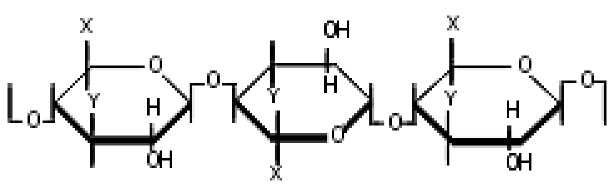
| SORT OF FOLIAGE | MASS | VOLUME OF ABSORBED OIL | PER GRAMM FOLIAGE |
|---|---|---|---|
| PLANE | 5g | 35ml | 7ml |
| LIME | 5g | 35ml | 7ml |
| MIX FROM BUILDING YARD | 5g | 35ml | 7ml |

The fact, that the foliage collected by the building yard absorbs as much oil as pure plane or lime leaves tells us that the percentage of bad absorbing plants must be small enough, that it has no effect on the mix.

## 3.2 Optimization

Now that the basics of our products were clear, we were able to optimize it. When we started our project we totally disregarded the expense factor. But in order to make our oil bonding agent profitable we had to reduce the costs. So that was the main issue we had to focus on in our second experiment serial.
To keep the expense factor as small as possible we decided to search for a different additive with the same qualities but cheaper. Increasing our knowledge about cellulose ethers we found out, that the methyl cellulose we used had an average molar mass of 60000g/mol and that with sinking molar mass the cellulose ethers become less expensive but also become less effective. So we ordered a small amount of methyl hydroxy propyl cellulose (MHPC: 45000g/mol) and of methyl hydroxy ethyl cellulose (MHEC: 40000g/mol).

We used our old recipe 7 parts foliage to 1 part additive to test our new materials. We only exchanged the 1 part with the new MHPC and MHEC and compared it’s efficiency to our old product. All of them could absorb 7ml of paraffin oil. So we decided to take the cheapest variety, the MHEC as our new additive. In all further experiments we used MHEC. Here an extract of its chemical structure:



$X = H_2C - O - R$ R = Alkylrest
$Y = O - R$

The nonpolar alkyls make the whole molecule hydrophobic and therefore make a composition with foliage resistent for the ingress of water. But the polar hydroxyl groups make it slightly hydrophilic. That allows us to use hot water as a cheap solvent to combine the additive (dry powder) with the leaves.

Now, with the new additive, we repeated the old experiment series and continued with more, cheaper mass ratios. Most important results in a table:

| MASS RATIO | MASS | VOLUME OF ABSORBED OIL | PER GRAMM BONDING AGENT |
|---|---|---|---|
| **1:1 Lime – MHEC** | 10g | 40ml | 4ml |
| **2:1 Lime – MHEC** | 10g | 50ml | 5ml |
| **5:1 Lime – MHEC** | 10g | 65ml | 6,5ml |
| **7:1 Lime – MHEC** | 10g | 70ml | 7ml |
| **8:1 Lime – MHEC** | 10g | 70ml | 7ml |
| **20:1 Lime – MHEC** | 10g | 70ml | 7ml |
| **30:1 Lime – MHEC** | 10g | 70ml | 7ml |

It is evident that the oil bonding ability only increases to a mass ratio of 7:1. It must be the maximum bonding capacity a lime based bonding agent can reach. All further experiments conduced to cost reduction. We couldn’t continue this series endlessly because the decreasing apparent densitiy set a boundary. We decided to stop at 30:1 and take that mass ratio for our product. It is a good compromise between bonding ability, expense-factor and apparent density. This was it. The product was finished.
Now we had to focus on how we could mass produce it.

## 4. Comparison

But first, we thought it might be interessting to know our products’ opponents. If we wanted that somebody will ever use our bonding agent, it had to be at least comparable to the business competition. So we used our gadget to compare the efficiency of our product with some established bonding agents:

Comparison:

| BONDING AGENT | MASS | VOLUME OF ABSORBED OIL | PER GRAMM BONDING AGENT |
|---|---|---|---|
| **Our Product** | 5g | 35ml | 7ml |
| **Antipestol III** | 5g | 35ml | 7ml |
| **EKOPERL 66** | 10g | 35ml | 7ml |
| **UNI-SAFE** | 10g | 15ml | 1,5ml |

You can see, that our product is absolutely competetive concerning the bonding ability.

With that good result, we compared the apparent density, too:

| BONDING AGENT | APPARENT DENSITY |
|---|---|
| **UNI-SAFE** | 420 Gramm per litre |
| **ÖKO-Pur Pulver** | 210 Gramm per litre (from literature) |
| **Our Product** | 145 Gramm per litre |
| **EKOPERL 66** | 80 Gramm per litre (from literature) |
| **Antipestol III** | 65 Gramm per litre |

Our product is in the normal range but even better than our two main rivals EKOPERL 66 and Antipestol III. These two are the most used bonding agents in Germany.

# 5. Out of the Laboratory

In our theory, the consumer can also be the producer. That means that we think that all the building yards in Germany have the equipment and the raw material (except for the additive) to produce their bonding agent on their own. We decided to create a manufacturing process with only simple technology.

## 5.1 Manufacturing Process

Winter 2004 the building yard of our hometown Metzingen promissed to cooperate with us in order to produce our bonding agent on a large scale. Next fall, when when there was again plenty of our raw material, we went to the building yard and asked for their help.
Instead of composting the collected leaves, they provided us with about six tonnes of foliage. After two more weeks, when the greenery was dry we began to fabricate our product. We didn't take all the six tonnes but used only  three tonnes. We were surprised how generous the building yard handled his foliage. It seemed they really wanted to get rid of it.

First we had to chaff our raw material roughly so that we could mix it with the additive. The shredder we used was a former garbage truck that is now used to produce wood chips.

We combined the foliage with 100 kilos of MHEC by using a wheel loader. We could have optimised the process if we would have used a cement mixer. Unfortunately the building yard Metzingen couldn’t lend us one at that time. The wheel loader had the same effect, but it took a bit longer.

After some time of mixing we activated our additive by using hot steam. It gave the loose mixture the consistency of a highly viscous pap.
Then we had to wait until it was dry again. It took about two weeks of storage in a heated hall. Now the mixture was hard and stiff. We used

another smaller shredder and hackled the pap until it was granulate. Now we only had to fill the bonding agent into bags and we were done.

We also distributed some bags to our local fire department, the building yard and an independent gas station to let them check the quality of our oil bonding agent. All of them were pleased with the efficiency and the fire department even gave us a report that proves their contentment.

We made it to fabricate our product in a large scale (three tonnes) only by using primitive technology. Now we only had to find out how expensive the process was.

## 5.2 Economical View

Especially building yards, the fire department, gas stations and maintenance depots need oil bonding agents from time to time. A big advantage of our product is that the building yards are able to produce it on their own as we proved with our manufacturing process. That means that the building yard needn't buy but could produce his own bonding agent. This allows us to compare the cost of production of our product with the sales costs of the established oil bonding agents.

The building yard would profit most because he anyway has to collect the foliage. But we haven't even considered this cost reducing factor in our calculation. We focussed mainly on the costs for labor, the machines and the material. We developed a cost calculation for the production of 516,6kg of our oil bonding agent based on our former manufacturing process:

Cost Calculation of our oil bonding agent
(example of building yard Metzingen)

| dry, grind | → | 16,6kg MHEC | → | steam | → | dry, grind |
|---|---|---|---|---|---|---|
| 40€ per 500kg | | ~116€ | | 112€ | | 112€ |

As you can see the production of 516,6kg oil bonding agent costs 380€. That would be 0,73€ per kilogramm.

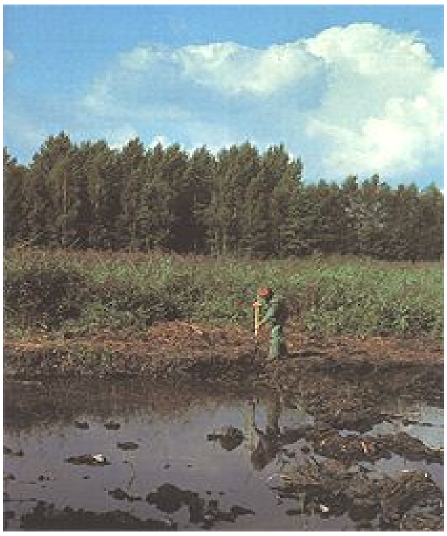
Comparison with established bonding agents:

| BONDING AGENT | MASS | BONDING ABILITY | PRICE |
|---|---|---|---|
| **Our Product** | 1kg | 7 litres | 0,73€ |
| **Antipestol III** | 1kg | 7 litres | 0,94€ |
| **EKOPERL 66** | 1kg | 7 litres | 1,95€ |
| **UNI-SAFE** | 1kg | 1,5 litres | 13,80€ |

The costs of production of our product underprices the sales costs of the other bonding agents a lot.

## 5.3 Ecological View

But not only the economic advantage makes our product a serious alternative to the established ones, but the ecological attribute, too. Some of today's used oil bonding agents have great disadvantages concerning their einvironment friendliness.



The widespread bonding agents Antipestol III and Elcosorb which were used by the buildig yard and fire department of Metzingen, too are made out of peat. To get this material one of a kind biotopes are getting destroyed. Through the immense cutting of peat some animal races and plants like the sundew are already endangered of extinction.
Several environmental protection organisations have declared peat cutting a threat to nature and boycott therefore goods made out of peat. There are only few of Europe's great highmoors left which we think should be protected.

Another oil bonding agent that is used very often is EKOPERL 66, a product based on foam-filled plastics. A huge disadvantage of EKOPERL is his low apparent density and therefore its sensitivity for wind. Once blown away, these synthetics stay out there in the nature.
Our product in contrast to that is 100% bio-degradable.

All in all we can say we succeeded in creating an efficient, profitable and environment-friendly oil bonding agent based on the waste material foliage.

## 6. List of Literature

[1] Gemeinsames Ministerialblatt No. 18, Bonn (1990); 41. volume p. 333
[2] Linder Biologie, Metzler, p. 47
[3] Römpp Chemie Lexikon
[4] Supplement of Clariant

## 7. We thank…

After having finished our project there are several people we really want to thank:
- Dr. Gminder from Albon-Chemie for giving us 50kg methyl hydroxy ethyl cellulose for free
- Mr. Bohn, our chemistry teacher, who always helped us with his knowledge and useful hints
- Mr. Eberhard Müller, director of the building yard Metzingen and his staff members who helped us producing our bonding agent in a large scale
- Mr. Brandt, our principal, for his financial aid
- Dr. Friedrich-Mackensen and the Bundesumweltwettbewerb-Team for giving us such a great opportunity