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## PREVENTING DECOMPOSITION OF AGRICULTURAL CHEMICALS BY ALKALINE HYDROLYSIS IN THE SPRAY TANK

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### INTRODUCTION

The effectiveness of an agricultural chemical against a target pest can be influenced by many factors, including sprayer calibration, rate of application, timing, temperature, rainfall, and the suitability of the chemical to its purpose. An additional factor that can influence the activity of a chemical is the pH of water used as a carrier during application. Many compounds that are used in fruit production are quite stable under a range of pH conditions. However, a number of them are unstable in alkaline water and break down via a chemical reaction called alkaline hydrolysis. For most compounds, the rate of alkaline hydrolysis is slow enough that significant breakdown does not occur under normal field conditions. However, even chemicals that decompose fairly slowly can experience some loss of activity if allowed to sit in the tank for too long (e.g. overnight) at high pH. With very sensitive compounds, the rate of alkaline hydrolysis can be so rapid that substantial breakdown occurs between the time of mixing and the time of application. To avoid degradation of chemicals in the spray tank, it is important to know the pH of your water source, and how the compounds that you apply react under alkaline conditions.

In this publication we describe the alkaline hydrolysis reaction and the conditions under which it occurs, and provide information on the susceptibility of agricultural chemicals commonly used in tree fruit production to this problem. In addition, data are presented on the pH of spray water sources in the major fruit growing areas of New York. Finally, we discuss ways to measure pH, and how to lower the pH of alkaline water to slow or prevent pesticide breakdown in the spray tank.

### WATER PH

pH is a scale that expresses the concentration of hydrogen ( $H^+$ ) ions in a solution (Fig. 1). The numbers (1-14) represent the negative log of the hydrogen ion concentration. Water is alkaline when it has a pH greater than 7. Factors that determine the pH of a body of water include the type and quantity of dissolved minerals and gasses, chemical reactions between the compounds in solution, and the products of photosynthesis and respiration from the microbial flora in the water. Dissolved carbonates and bicarbonates are probably the most important factors contributing to the alkalinity of a water source. The compounds present, and reactions occurring in water can be altered by temperature, rainfall and runoff, and activities such as lime or fertilizer applications in the watershed of a pond or stream. As a result of the number and variability of the contributing factors, water pH is not a constant, and can be expected to change over the course of the season.

Another factor that is important in determining the extent to which a compound will break down in the spray tank is the buffering capacity of the water. Buffering capacity is the ability of a solution to resist changes in pH when acidic or alkaline substances are added. A buffer system consists of several compounds interacting in a chemical equilibrium. The compounds interact by either reacting with excess  $H^+$  or  $OH^-$  ions or contributing ions to the system to maintain a particular pH. The pH at which a buffered system reaches equilibrium (and tends to stay) depends on the compounds that are participating in the system. Many compounds commonly present in water can contribute to a buffer system.

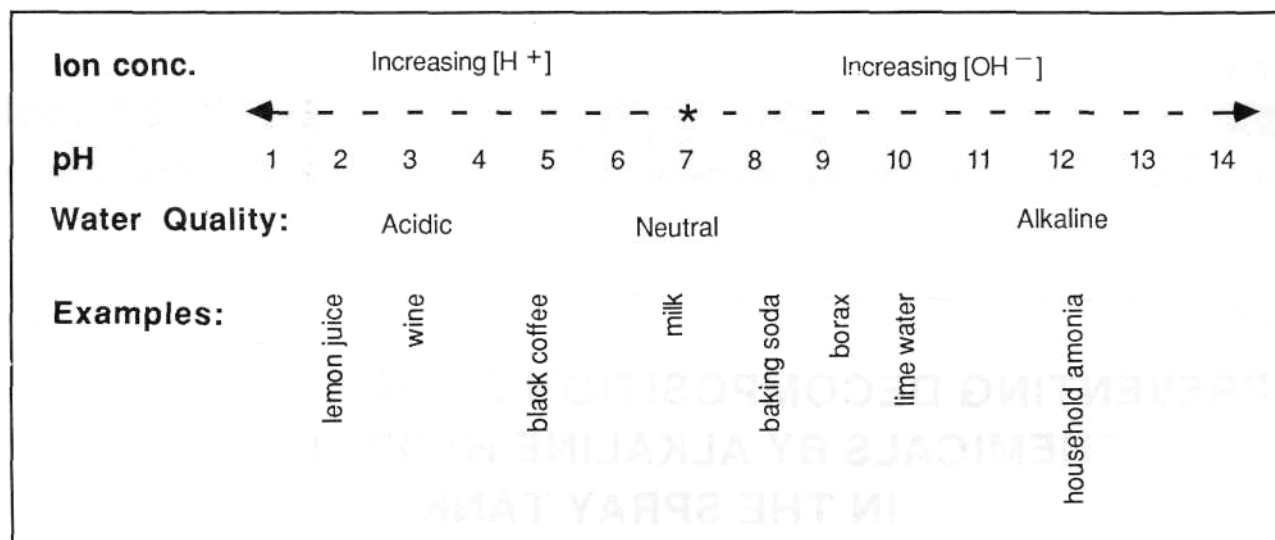


Figure 1.

### ALKALINE HYDROLYSIS

The chemical reaction that is responsible for the degradation of agricultural chemicals in alkaline water is called alkaline hydrolysis. Hydrolysis is the decomposition or splitting of a compound by water in the presence of ions. Water that is alkaline or acidic has a larger concentration of active hydroxide ( $OH^-$ ) or hydrogen ( $H^+$ ) ions, respectively, than water that is neutral. The rate of hydrolysis increases with increasing ion concentration. Consequently, the rate of alkaline hydrolysis increases with increasing pH (increasing  $OH^-$  concentration).

The extent to which a compound will continue to undergo alkaline hydrolysis in a water solution depends on the buffering capacity of the water. In an unbuffered solution, hydroxide ions would be consumed during the hydrolysis reaction, and the reaction would slow and eventually cease as the hydroxide ion concentration decreased. In a buffered system, hydroxide ions consumed by the reaction would be replaced by the compounds that comprise the buffering system. In a solution with a large buffering capacity, it is possible that hydrolysis could continue until all of the compound is decomposed.

### SUSCEPTIBILITY TO ALKALINE HYDROLYSIS

In general, insecticides are more susceptible to alkaline hydrolysis than are fungicides and herbicides. Within the insecticides, the carbamates and organophosphates are generally more susceptible than the chlorinated hydrocarbons and pyrethroids. Table 1 presents information on the susceptibility of many of the agricultural chemicals commonly used in tree fruit production to alkaline hydrolysis. Information is presented in the form of a "half-life" when possible. The

half-life of a compound is the amount of time it takes for half of the material to break down at a particular pH. For example, half of the active ingredient of phosmet (Imidan) will decompose after 3 hours at pH 8.3, while at pH 10 it takes only one minute to lose half the active ingredient. Chlorpyrifos (Lorsban), by contrast, has a half-life at pH 8 of 22 days, and is one of the more stable insecticides. It should be noted that in most of the experiments conducted to determine the half-life of these compounds the technical material rather than the formulated product was tested. Adjuvants used in the various formulations tend to increase the stability of a compound in solution. Consequently, the half-life estimates in Table 1 are probably shorter than the actual half-life of the formulated material.

### PH SURVEY

A survey of the pH of spray water sources in four of the major fruit-growing areas of New York was conducted in 1984 and 1985. Fifteen to 20 sites were sampled in each area during three separate sampling periods: summer, fall, and spring. The pH of the samples was analyzed soon after collection, using a portable, electronic pH meter (Fisher Model 107, accurate to 0.03 pH). Samples of 125 ml of water were collected at the same sites during each sampling period. The results, summarized for each area, are presented in Table 2.

The pH of spray water sources in the areas surveyed was very similar in terms of overall mean and range during the time the survey was conducted. The western Hudson Valley differed from the other areas in that it was the only area that consistently had sites with pH values below 7.0, which resulted in a wider range of values for this area. Table 3 presents data pooled within sampling period from all sampling areas. A sub-

**Table 1. Susceptibility of commonly used agricultural chemicals to alkaline hydrolysis.**

Brand name	Common Name	Class	Half Life
Ambush	permethrin	PY	Stable at pH 6-8. Less soluble at high or low pH.
Cygon	dimethoate	OP	Generally unstable in alkaline media. Optimum pH between 4 and 7.
Diazinon	diazinon	OP	pH 4.5 - 0.45 weeks pH 5.0 - 2.0 weeks pH 7.0 -10 weeks pH 8.0-2.7 weeks
Ethion	ethion	OP	pH 8.0-8.4 weeks pH 9.0 -17.8 days
Guthion	azinphos methyl	OP	pH 5.0 -17.3 days pH 7.0-10 days pH9.0 -12 hours
Imidan	phosmet	OP	pH 7.0 -1 day pH 8.3 - 4 hours pH 10.0-1 minute
Lannate	methomyl	CB	pH 6.0 - 54 weeks pH 7.0 - 38 weeks pH 8.0 - 20 weeks
Lorsban	chlorpyrifos	OP	pH 4.7 - 63 days pH 6.9 - 35 days pH 8.1 - 22 days
Malathion	malathion	OP	pH 6.0 - 7.8 days pH 7.0 - 3.0 days pH 8.0-19 hours pH 10.0 -2.4 hours
Mitac	amitraz	FA	pH 5.1 -1.26 hours pH7.1 -15 hours pH 9.2 - 35 hours
Morestan	oxythioquinox	OH	Stable under field conditions
Nudrin	methomyl	CB	39% loss after 6 days at pH 9.1
Parathion	parathion	OP	pH 7.0 -120 days  pH 10.0-29 hours
Pay-off	flucythrinate	PY	Generally stable in solution
Pennacap-M	methyl parathion	OP	Hydrolyzes several times faster than parathion
Phosdrin	mevinphos	OP	pH 7.0 - 35 days pH 11.0-1.4 hours

Phosphamidon	phosphamidon	OP	pH 4.0 - 74 days pH 7.0-13 days pH 10.0-30 hours
Pounce	permethrin	PY	Stable at pH 5.7 - 7.7 11% loss after 42 days at pH 9
Pydrin	fenvalerate	PY	Very stable at pH 5-9
Sevin	carbaryl	CB	pH 7.0 - 24-30 days pH 8.0 - 2-3 days pH 9.0 -1 day
Thiodan	endosulfan	CH	70% loss after 1 week at pH 7.3-8.0
Vydate	oxamyl	CB	Stable at pH 4.7 3% loss after 24 hours at pH 6.9 45% loss after 24 hours at pH 9.1
Zolone	phosalone	OP	Stable at pH 5-7 112 life 9 days at pH 9
<u>Miticides</u>			
Carzol	formetanate	CB	pH 5.0-4 days pH 7.0-14 hours pH 9.0 - 3 hours
Kelthane	dicofol	CH	pH 5.0 - No degradation after 20 days pH 7.0 - 5 days pH 10.0 -15 minutes
Omite	propargite	OC	pH 3.0-17 days pH 6.0 - 331 days pH 9.0 -1 day
Plictran	cyhexatin	OT	Extremely stable
Vendex	fenbutatin-oxide	OT	Compound extremely stable; Formulation forms suspension, not solution, with water

#### Plant Growth Regulators

Alar	daminozide
Ethrel	ethephon

#### Fungicides

Bayleton	triadimefon	TZ	Stable over a wide range of pH
Benlate	benomyl	BZ	Susceptible to alkaline hydrolysis: specific information not available

Captan	captan	PT	pH 4.0 - 32.4 hours pH 7.0 - 8.3 hours pH 10.0-2 minutes
Funginex	triforine	PZ	Stable to pH 10 or 11
Rubigan	fenarimol	PD	Stable over a wide range of pH

Key to classes:

BZ	benzamidazole
CB	carbamate
CH	chlorinated hydrocarbon
FA	formamidine
OC	organic compound
OH	organic hydrocarbon
OP	organophosphate
PD	pyrimidine
PT	phthalimide
PZ	piperazine
PY	pyrethroid
OT	organotin compound
TZ	triazole

stantial proportion (from 30-48%) of the sites had pH values above 8.0. Water at this pH could cause problems for compounds such as ethephon (Ethrel) or daminozide (Alar), which can hydrolyze in only slightly alkaline water. Compounds that undergo hydrolysis at a moderate rate at this pH, such as formetanate-hydrochloride (Carzol) and Imidan should be applied soon after mixing to minimize losses in the spray tank. A smaller proportion (9-22%) of sites had pH values above 8.5. Above this level, the rate of alkaline hydrolysis becomes rapid enough for compounds such as Carzol and Imidan that substantial breakdown could occur in the tank if there is any delay in spraying the tank once it is mixed. A few sites (2-13%) had pH values above 9.0 during one or more of the sampling periods. At this pH, compounds such as azinphosmethyl (Guthion) or malathion, which would not undergo significant breakdown in most situations, may have problems. Again, the buffering capacity of the water plays an important role in determining the amount of the active ingredient that decomposes. A weakly buffered water source at a high pH would pose less of a problem than water with a high pH and a large buffering capacity.

One additional point that should be noted in these data is the degree of seasonal variability that can occur at one site (Table 4). Some sites had differences of nearly two pH units between sampling periods. We did not, however, detect greater variability in surface water

sources when compared to ground water sources, or any difference in the average pH between these two types of water sources.

### PREVENTING ALKALINE HYDROLYSIS

The first step in preventing loss of activity due to alkaline hydrolysis is to determine the pH of water used for mixing chemicals. Because of seasonal variability, it is important to measure the pH several times over the course of the growing season. Samples should be collected in a clean, nonreactive container, such as a glass bottle or jar. The water collected should be representative of the water used for spraying. For example, when taking a sample of water from a tank or well, let the water run long enough to flush water that has been standing in a hose or pipes. When collecting from a pond, try to take a sample near where the water is usually pumped. It is important to determine the pH of the sample soon after collection, because the pH of water can change if it is stored too long.

The most accurate method of measuring pH is to use an electronic pH meter. However, they are expensive, and not very practical for field use. A less accurate method involves the use of dyes that change color in response to pH. These dyes are available in the form of paper strips, or in solution for use in soil pH test kits. Soil test kits can be used to test water pH. A few drops of the indicator solution is mixed with a small amount

**Table 2. pH of water sources in fruit growing areas of New York.**

	Mean	Range	% ≥8.0      ≥8.5      ≥9.0		
<u>Champlain Valley (15)*</u>					
Summer 1984	7.72	7.05 - 8.50	27	7	0
Fall 1984	8.11	7.30 - 9.15	60	20	13
Spring 1985	8.05	7.25 - 9.25	47	7	7
<u>E. Hudson Valley (13)</u>					
Summer 1984	7.86	6.65 - 8.60	54	23	0
Fall 1984	7.68	7.20 - 8.05	31	0	0
Spring 1985	8.07	7.20 - 9.25	54	23	15
<u>W. Hudson Valley (11)</u>					
Summer 1984	7.92	6.60 - 8.30	18	0	0
Fall 1984	7.71	6.90 - 8.55	27	18	0
Spring 1985	8.32	6.45 - 9.25	55	45	27
<u>Wayne County (15)</u>					
Summer 1984	7.82	7.35 - 9.40	20	7	7
Fall 1984	No sample taken				
Spring 1985	8.07	7.35 - 9.85	40	20	13

\*Numbers in parentheses represent the number of sites sampled in each area.

**Table 3. Proportion\* of sites with high pH.**

	% ≥8.0      ≥8.5      ≥9.0		
Summer 1984	30	9	2
Fall 1984	41	13	5
Spring 1985	48	22	13

\*Of 54 sites sampled.

**Table 4. Seasonal variability in spray water sources.**

Source	Summer 1984	Fall 1984	Spring 1985
spring	7.55	7.45	8.15
brook	7.65	8.00	8.15
brook	8.05	8.10	8.35
well	8.00	8.45	7.95
stream fed pond	7.60	7.75	7.95
well	7.85	8.70	7.85
artesian well	7.85	8.10	8.25
tank from pond	7.30	9.15	7.55
well	7.30	7.35	7.85
stream to tank	7.85	7.80	8.20
pond	8.50	7.75	7.95
lake	7.40	8.35	8.35
town water	7.05	7.30	7.25
drilled well	8.30	8.35	7.80
pond	7.60	9.10	9.25

of water in the well on the spot plate where the soil is usually placed. Sources for pH indicator papers and soil pH test kits are listed at the end of the paper. Instructions for their use are included in the kits. In general, the indicator is mixed with or dipped into the water, and the resulting color is compared to a standard color chart. It is often necessary to do a preliminary test with a wide range indicator included in the test kit to make a rough estimate of the pH. An indicator with a narrower range is then used for a more precise determination.

To minimize the possibility of break-down of chemicals in the tank, it is good practice to apply a spray right after it is mixed. However, this is not always possible. For instance, sudden weather changes may cause a delay or interruption of the spraying operation, and the tank mix may sit for an unacceptable length of time. If this occurs, a buffering agent may have to be added to the tank if the pH is high and the chemical in the tank is susceptible to alkaline hydrolysis. Buffering agents are available from many distributors of agricultural chemicals. Some of the foliar nutrient solutions also have buffering capabilities. These products work by lowering the pH, and providing a buffering system to maintain that pH. Many insecticides are most stable in solution at pH 4-6.

Buffering agents should also be added to tank mixes of extremely susceptible chemicals if the pH of the water is high enough that substantial decomposition could occur in the length of time it normally takes to empty a tank. Note that tank mixes containing fixed copper fungicides, such as Bordeaux mixture and copper oxide should not be acidified. Copper is more soluble under acidic conditions, and the resulting high concentrations can cause phytotoxicity.

Incompatible tank mixes can also cause loss of activity due to alkaline hydrolysis. Susceptible materials should not be mixed with lime, sulfur, liquid ammonia, or other materials that raise the pH of the solution. Product labels, and the tech sheets available from chemical manufacturers are often good sources of information about incompatibility and susceptibility to alkaline hydrolysis. Always read the label before mixing and applying agricultural chemicals to insure that they are being used with maximum safety and effectiveness.

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## SOURCES FOR PH TESTING MATERIALS

### PH INDICATOR PAPER

Ward's Natural Science Establishment  
PO Box 1712 Rochester, NY 14603

VWR  
PO Box 1050  
Rochester, NY 14603

Fisher Scientific PO  
Box 8740 Rochester,  
NY 14642

### SOIL PH TEST KITS

Agronomy Soil Test Laboratory  
804 Bradfield Hall  
Cornell University  
Ithaca, NY 14853  
(tests in the pH range 4.0-8.6)